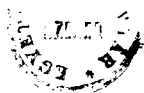


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REDIGIT:

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## THE MINERALS OF THE SULPHIDE ORE-DEPOSIT OF NAGYBÖRZSÖNY

By S. KOCH and GY. GRASSELLY

Recent literature dealing with this mining district involves merely the work of K. Sztróka<sup>1</sup> concerning the solution of the wehrnite problem,<sup>1</sup> a short topography of F. Papp<sup>2</sup> and the interesting mining geological and genetical publications of G. Pantó.<sup>3, 4</sup>

At the present, only exploitation is in progress at Nagybörzsöny the lodes being only opened up to a small extent. In spite of this the material obtained provided material for interesting observations. It is anticipated that when later on the ore and non ore-minerals will be obtained more abundantly it will be possible to supplement these observations.

On the basis of the communications of G. Pantó it is known that the ore occurs in impregnated zones in highly caolinitised biotite-amfibolite and in its agglomeratic associated rocks, forming veins in the propylitized biotite-amfiboleandezite. According to him two orebearing phases can be differentiated. At very high temperature the main product of the first phase was pyrrhotite which was in the first place transformed still at a fairly high temperature in the second orebearing phase.

In the Middle Ages the most significant mining took place in the lodes extending at the depths of the Rózsahegy, these lodes, were opened up through the mines of Fagyosasszony, Alsó- and Felsőrózsabánya. In Modern Times no significant mining is carried on in this district. However, the samples obtained at the recent exploitation show that Nagybörzsöny is from the genetical point of view one of the most interesting and also one of the richest mining districts of Hungary.

The ore of the lodes is compact showing only smaller cavities. The ores and the accessory minerals occurred hitherto only in quite rare instances in larger overgrown crystals. The mineralassociation is abundant in species as illustrated by the following enumeration:

The oldest minerals:

apatite, quartz, pyrite I., galena I., pyrrhotite, valleriite, sphalerite I., chalcopryrite,

younger minerals, partly formed from  
the material of the older ones:

arsenopyrite, tetrahedrite, native bismuth, bismuthinite, native gold, galena II., cosalite, sphalerite II., jamesonite,

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the minerals of the oxidized zone:

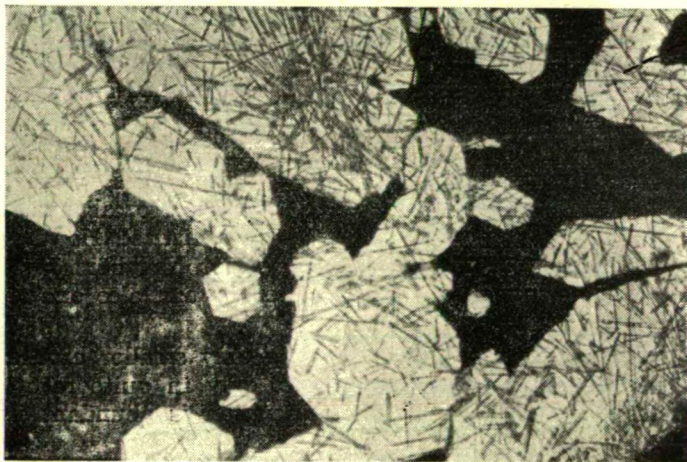
semseyite, tetradymite, (csiklovaite, hes-  
site, petzite, argentite, proustite, molyb-  
denite) barite, dolomite, calcite,

hydropyrite-melnikovitepyrite-pyrite II.,  
marcasite, siderite, magnetite, cronsted-  
tite, chalcocite, covellite, goethite, limo-  
nite, arsenolite.

The minerals enumerated in brackets were found by the above authors, however, those of the present paper could not detect them in their polished sections.

### Apatite

Apatite is the oldest mineral of the impregnated zones. It occurs as inclu-  
sions in quartz and the oldest ores in the form of fine needles in pneumatoly-  
tic hollows of volcanic rocks and not in the according to *c* tabular overgrown  
crystals occurring only rarely in hydrothermal lodes (Roznava). A crystalline  
quartz sample obtained from the immediate vicinity of the apatite content  
of the ore calculated on the basis of the determination of the  $P_2O_5$  content  
amounted to 0,59 per cent. In this crystalline quartz the apatite needles are  
arranged spherulitically, whereas in the crystallized quartz and ores its thin  
needle crystals can be detected arbitrarily scattered, or aggregated in larger  
numbers (microphoto 1.). Of the primarily separated ores pyrrhotite



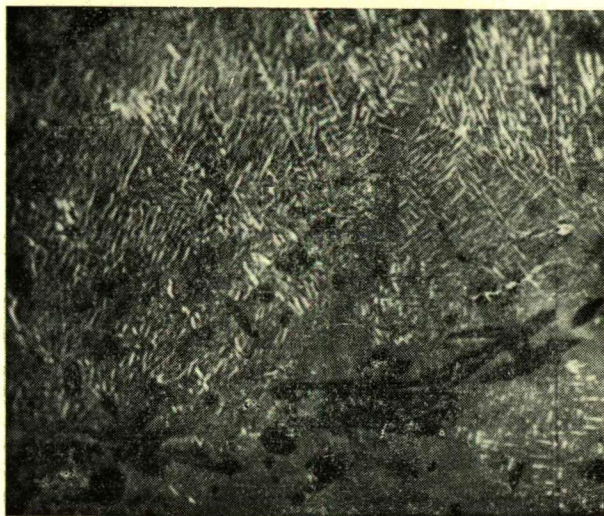
1.

Thin acicular crystals of apatite in crystallized  
quartz. 380 $\times$ , N ||

most probably also contained apatite but after the transformation of the sul-  
phide the apatite needles could no more be detected. The presence of apatite  
in sphalerite and chalcopyrite is a very interesting phenomenon. The small  
apatite needles contained in sphalerite were detected associated with a dis-  
mixtured chalcopyrite lamellae system (microphoto 2.) and those con-  
tained in chalcopyrite associated with tiny sphalerite stars (microphoto

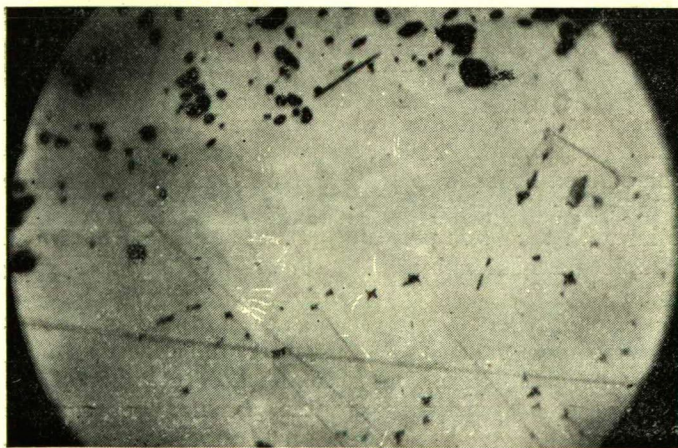


3.). In arsenopyrite the ore surrounding the quartz crystals is crowded with fine apatite needles. The occurrence of apatite in these ores points to them being formed at an unusually high temperature.



2.

Apatite needles in sphalerite with dismixture of lamellated system of chalcopyrite.  
Oel imm. 450.  $\times$ , N  $\parallel$



3.

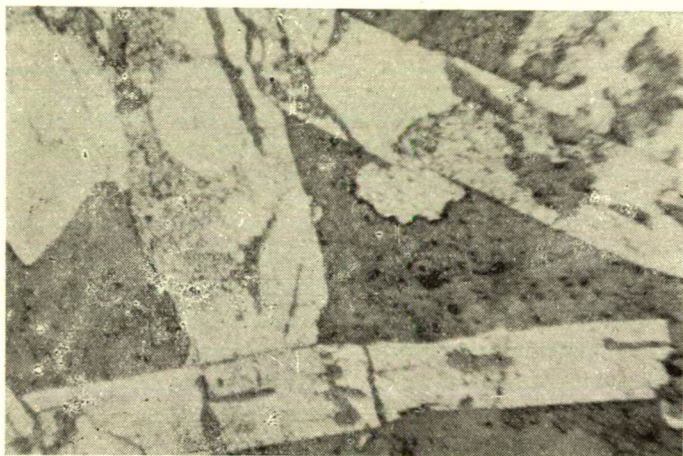
Apatite needles in chalcopyrite with sphalerite stars.  
Oel imm. 450  $\times$ , N  $\parallel$

Pyrrhotite and the minerals formed from it

Of the once dominating ore — pyrrhotite — only fragments containing either syngenetic or somewhat older idiomorph, but strongly corroded hexa-



hedral crystals of the first generation of pyrite can be found. In comparison to the dominating pyrrhotite the amount of pyrite must have already originally been slight. In addition to pyrite the rounded or elongated oval inclusions of galena I. could also be detected in pyrrhotite. Rendering it probable that this ore had still had an older generation formed in the early stages of ore-formation. The mostly altered pyrrhotite has a lamellar tabulated structure. Its roselike aggregates formed by parallel intergrowths of some welldeveloped finely tabulated crystals a few mm in size are overgrown on the walls of the small hollows of the ore. The pyrite pseudomorphoses a few cm in size contained in the collection of the Hungarian Geological Institute prove that pyrrhotite also occurred in larger crystals.



4.

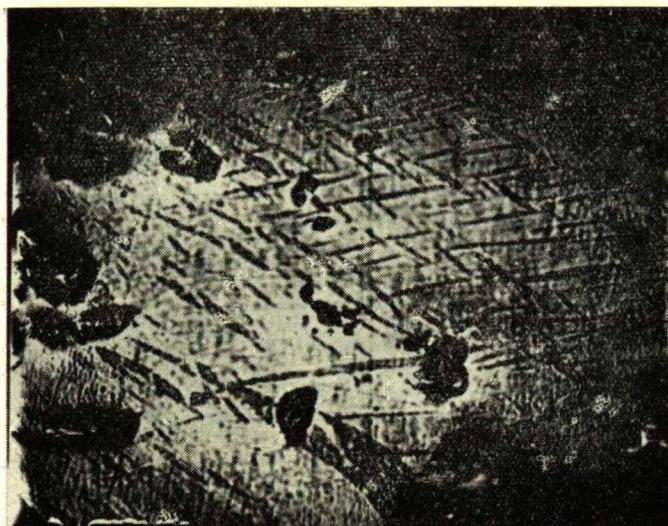
Pyritized pyrrhotite lamellae. 200  $\times$ , N II

Our polished sections contained a great number of lamellae and lamellated pyrrhotite aggregates one mm in size, partly or quite transformed into pyrite and surrounded by siderite (microphoto 4.). In the lamellae numerous thin long spindleformed ingrowths of the „light” component — often running parallel with the basis platelets — could be detected. On air etching a pyrrhotite sample permeated by gelpyrite showed an interesting structure (microphoto 5).

The dark coloured platelets arranged according to definite crystallographical directions corresponded to the „lighter” component, the presence of which could also be observed on the sample before etching. A translatio phenomenon observed on a pyrrhotite granule polished perpendicularly to the basis showing a lamellar structure was most interesting. Among the strongly curved pyrrhotite lamellae products of the alteration could already be detected (microphoto 6.). It deemed of no interest to analyse this pyrrhotite as even its smallest granule was not homogenous, however, it could be established that it did not even contain in spectroscopically detectable traces nickel. An analysis of the metal content of a sample collected from the waste tip of Alsó-Rózsabánya containing mainly iron-sulphides and rich in ore shows the following results:

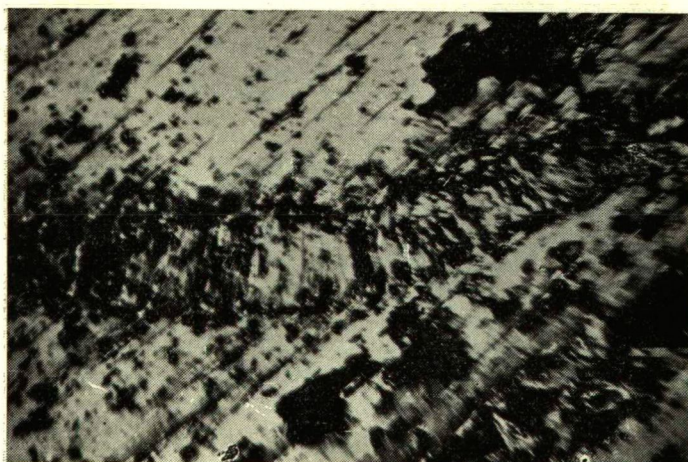


Fe .....	46,19%
Cu .....	1,97
As .....	4,85
Zn .....	2,00
Pb .....	traces



5.

Etching figures on pyrrhotite performed by  
air etching. Oel imm. 400  $\times$ , N  $\parallel$

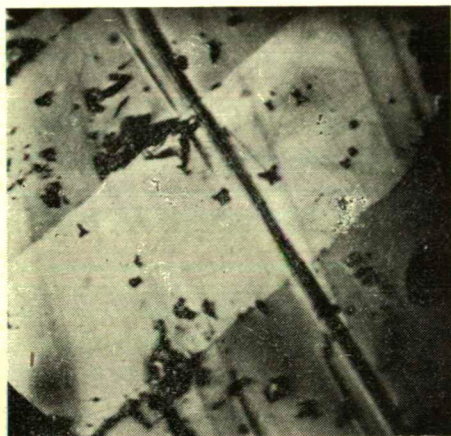


6.

Translation of pyrrhotite lamella, perpendicular  
to the plate (0001). 200  $\times$ , N  $\parallel$

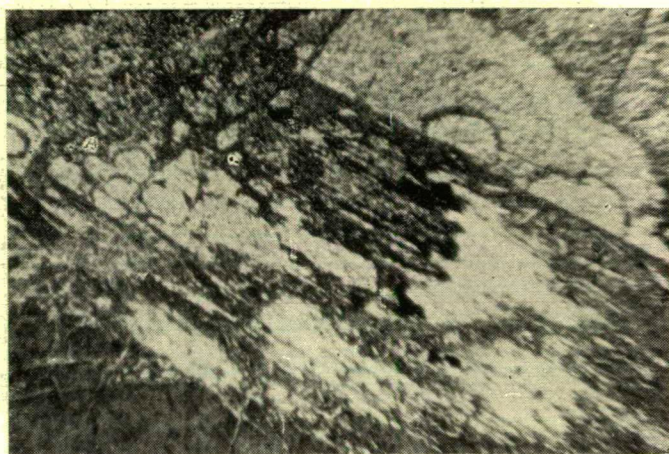
Of the ores syngenetic with pyrrhotite both sphalerite and chalcopyrite play a role in replacing it. Pyrrhotite is lamellarly replaced by chalcopyrite in which sphalerite stars can be detected (microphoto 7.). The readily

decomposing pyrrhotite is interwoven and surrounded at the border of the granules along the cleavage direction by the iron-sulphides formed from it in the oxidized zone (microphoto 8.). These secondary ores have a gel structure which varies considerably, at numerous sites fine bird eyes can be



7.

Chalcopyrite replacing pyrrhotite  
with sphalerite stars.  
Oel imm. 400  $\times$ , N  $\parallel$



8.

Pyrrhotite lamella replaced by secondary  
iron-sulphides. 160  $\times$ , N  $\parallel$

discovered (microphoto 9.). In the pyrrhotite as well as in the gel the „intermediate product” mentioned by Ramdohr showing a strikingly strong interference phenomenon could be detected. This „intermediate product” extended in the cleavage direction of the pyrrhotite in thin bands, or it could be found as small patches in the gel.

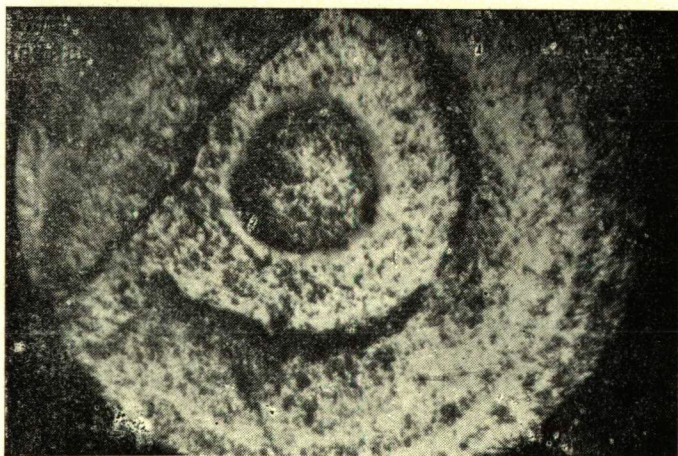


Among the alteration products the very compact, badly polishable very finely granulated hypopyrite showing between crossed nicols a quite dark colour, melnikovitepyrite with a varying gel structure and the finely granulated pyrite in which exquisite bird eyes could be found occurred (micro-



9.

Gel structure in secondary iron-sulphides. 200  $\times$ , N ||



10.

Birds eye structure. 200  $\times$ , N ||

b h o t o 10.). These intermediate products lead to the formation of the coarsely granulated pyrite II. and marcasite surrounding often the latter at the border of its crystal aggregates, but, sometimes also penetrating into it.

The intermediate products ranging between  $\text{FeS} - \text{FeS}_2$  are so much interwoven that it is very difficult to select even grossly homogeneous samples for chemical investigations. The filtrate of an on the whole homogeneous dark grey colour compact hypopyrite sample treated for ten minutes with N hydrochloric acid contained:

12,91 per cent Fe  
3,13 per cent SO<sub>4</sub>.

An analysis of the residual substance after the treatment showed the following composition:

Fe .....	27,94%
Cu .....	0,90
As .....	3,15
Mn .....	0,13
Sb .....	trace
Co .....	0,01
S .....	32,44
Al <sub>2</sub> O <sub>3</sub> .....	3,55
CaO .....	0,81
MgO .....	0,48
insol. residue .....	0,02

Recalculating the sulphated iron-sulphide amount for sulphide merely taking the component elements of the sulphides into consideration and then calculating the results for 100 per cent:

Fe .....	52,04%
Cu .....	1,14
Mn .....	0,16
Co .....	0,01
As .....	4,01
S .....	42,64
<hr/>	
100,00%	

Subtracting from the result the amount of iron and sulphur needed for the formation of chalcopyrite and arsenopyrite, as well as that of sulphur treatment with hydrochloric acid we obtain:

Fe	48,06	0,8607	1
S	39,78	1,2403	1,44

thus the iron-sulphur relation is: Fe : S = 1 : 1,44.

On calculating for 100 per cent the residual substance gained after the treatment with hydrochloric acid we obtain:

Fe	27,94%	43,28%
Cu	0,90	1,39
Mn	0,13	0,20
Co	0,01	0,01
As	3,15	4,87
S	32,44	50,25
<hr/>		100,00%

and again subtracting the iron and sulphur amount needed for the formation of the above minerals the iron-sulphur ratio of the residual substance is:

$$\text{Fe} : \text{S} = 1 : 2,11$$

Thus in the course of the transformation the iron amount decreases and on the decomposition of the pyrrhotite lattice the iron evolving from the pyrrhotite lattice the iron evolving from the compound partly forms arsenopyrite, the greater part, however, is transformed into siderite interweaving densely the intermediary products. The crystals and crystalline aggregates of pyrite II. can be found embedded.

As already pointed out by G. Pantó in the course of decomposition a part of the iron content of pyrrhotite was taken up the younger arsenopyrite partly formed from it. The small idiomorph crystals and crystal aggregates of the latter crystallising readily can be found in the intermediate products mentioned above, less frequently they replace pyrrhotite lamellarly. In some sections its idiomorph crystals are surrounded by the crystal aggregates of the younger marcasite. Among crystal overgrowths, arsenopyrite is the most frequent ore, its crystals attain half a cm in size. The crystals are short columns plane forms (110), (101) and (001) could be detected on them. Very frequently parallel intergrowths in the  $b$  crystallographic axis direction, as well as sections with very fine twinned intergrowths according to (110) could be observed. Each of our electrographically etched polished sections showed the zone structure of arsenopyrite crystals. An analysis of the crystal overgrowths did not demonstrate any cobalt, however, this element could be found both electrographically and analytically in the crystalline granular aggregates, but always only in the younger crystal granules situated at the border of the aggregate. The crystalline granular aggregates also contained nickel in traces. Pyrrhotite less frequently sphalerite, are replaced by arsenopyrite, whereas pyrite II. in turn replaces the latter. Very fine pyrite pseudomorphoses after arsenopyrite could be found in the polished sections. An analysis of crystallised arsenopyrite is as follows:

Fe .....	33.09%
Mn .....	0.20
As .....	40.93
S .....	20.06
insol. residue .....	5.85
	<hr/> 100.13%

The fine small crystal overgrowths of siderite, a few mm in size, also formed from the iron contained in the pyrrhotite can be found in the oxidized zone in every polished section filling up the hollows and penetrating into the fissures of the ores. On the small crystals in our possession the following crystalforms could be established by goniometric measuring (according to order of magnitude):

(21 $\bar{3}$ 1) (11 $\bar{2}$ 0) (05 $\bar{5}$ 1) (0001) (10 $\bar{1}$ 1) (02 $\bar{2}$ 1) (01 $\bar{1}$ 2).

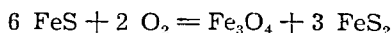
The greater part of the crystals show a scalenohedral habitus, beside the dominating (21 $\bar{3}$ 1), the small planes (11 $\bar{2}$ 0), (10 $\bar{1}$ 1), (02 $\bar{2}$ 1) and (01 $\bar{1}$ 2) could also be found. The minute crystals on which only planes  $-\frac{1}{2}R$  can be detected are rarer they have a saddlelike curvature. The crystals of the third type, one mm in size, are more thickly tabulated according to (0001) and in addition to the dominating basis planes planes (21 $\bar{3}$ 1), (11 $\bar{2}$ 0) and (05 $\bar{5}$ 1) can also be detected, on them the minute crystals form irregular intergrown aggregates. All three types are also known from Kisbánya (Herja, Roumania). The siderite of Börzsöny corresponds almost exactly as regards crystal form as well as composition to that found in Kisbánya of similar origin."



	Nagybörzsöny	Kisbánya	Calculated
FeO	61,07%	61,68%	62,01%
MnO	0,76	0,14	—
CaO	trace	0,08	—
MgO	trace	0,23	—
CO <sub>2</sub>	37,88	37,80	37,99
residue			
insol.	0,48	0,31	—
	100,19%	100,24%	100,00%

As can be seen the composition of both these siderites is very similar to the theoretical one. It is anticipated that as the mining proceeds larger and finer samples of this interesting mineral will be available.

J. Erdélyi was the first to observe the crystal aggregates of cronstedtite on a sample collected from the waste tip of Alsórózsabánya. The crystal aggregates were 1 mm, the crystals composing then still smaller, hardly 1 mm in size. On one sample belonging to the Geological Institute we also detected this phenomenon. We detected — also only on a single sample — a magnetite aggregate composed of minute octahedral crystals. According to Ramdohr at the transformation of pyrrhotite — pyrite, magnetite formed in the following way:

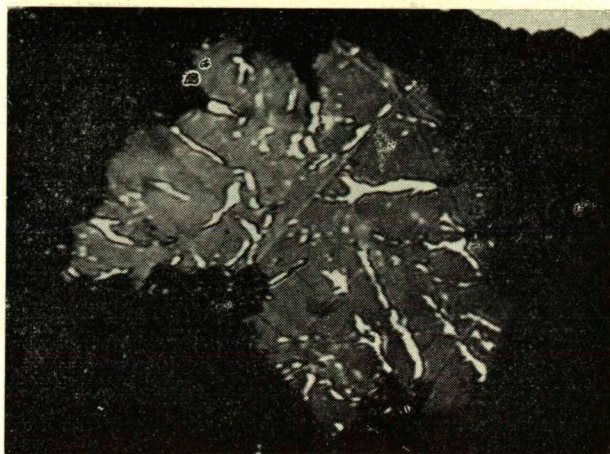


The dark brown velvetlike globules hardly one mm in size of needle iron ore consisting of fine threads could be observed as overgrowths on pyrite II. The surface of the disintegrated pyrite fragments is coated with ochreous limonite.

### Sphalerite

The sphalerite of Nagybörzsöny is like that of Kisbánya black and rich in iron. The internal reflexes demonstrated on polished sections have a red-brown — reddish colour. The well developed crystals one mm in size showing a crystalline granular structure can usually be detected overgrown on the walls of the hollows of the ore fragments or intergrown in the carbonateous basic substance. In the former platelet forms (111), ( $\bar{1}\bar{1}\bar{1}$ ), (100) could be found, platelets (111) dominating the greater part of the crystals are twins. The intergrown crystals show the same combinations of form, but the inverse tetrahedron and the hexahedron only can be observed in hardly detectable thin small bands. The sphalerite formed at very high temperature contains not unfrequently badly corroded remnants of older pyrite and pyrrhotite. These sphalerites are particularly rich in dismixtured products. The replaced pyrrhotite remains are lamellar, angular, whereas the pyrrhotite inclusions formed in the course of the dismixture are droplike, there order of magnitude being far below that of the replaced pyrrhotite fragments. In some of the chalcopyrite granules formed at the dismixture the plates and patches of valleriite are most conspicuous indicating that the chalcopyrite — valleriite system formed at a high temperature — unusual in the case of ore lodes of hydrothermal origin — and that its substance was originally chalcopyrrhotite, the two ores having formed at its dismixture. Valleriite contained irregularly or as plates in larger chalcopyrite granules and in smaller ones vermiform is very striking by virtue of its strong pleochroismus and its illuminating interference colours bet-

ween crossed nicols (microphoto 11.). Valeriite was detected by Helke<sup>27</sup> under quite similar conditions in Kisbánya (Herja), as well as by the present-writers on their own preparations.

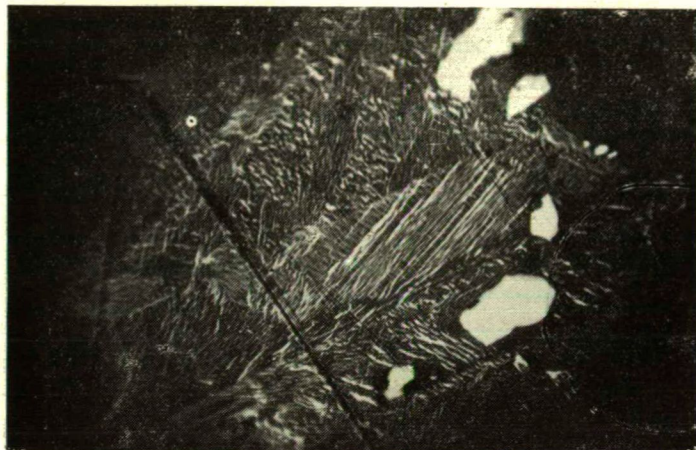


11.

Valleriite in sphalerite grain. Oel imm. 800 $\times$ , N ||

The sphalerite-chalcopyrite systems vary extremely. There is hardly a sphalerite in which a chalcopyrite inclusion cannot be found. The inclusions can mostly be detected on the borders of its crystal aggregates towards the middle they are far less frequent. It is interesting that at the points where sphalerite comes into contact with other sulphide ores chalcopyrite inclusions can be found in large numbers at the dividing line of the two ores. The chalcopyrite droplets of a few microns of order of magnitude undoubtedly produced by the dismixture, can often be found associated with plate systems usually divided according to crystallographic directions, the chalcopyrite substance of which extending according to crystallographic directions and also sometimes indicating the polysynthetic twin structure of the sphalerite can partly be interpreted by replacement (microphoto 12.) and partly by simultaneous separation or by oriented intergrowths. The repeated finding of chalcopyrite rows in marked zones in various sections seems to support the latter assumption. The inclusion systems cannot only be detected under the microscope, but also often with the naked eye, frequent by attain the size of one mm the different bands vary from 25—30 microns and those not attaining the microscopic field of vision. The photos are very much the same as those described by G. Pantó<sup>8</sup> of the sphalerites of the Mihály lode of Toroiaga, the only difference being that they vary to a far greater extent.

The small tetrahedral sphalerite crystals ingrown in the carbonateous quartzous substance also contain abundantly chalcopyrite inclusions, however, their iron content is already considerably less, as indicating the following analyses:



12.

Chalcopyrite lamellae system in sphalerite.  
Oel imm. 600 X, N ||

	crystalline granular sphalerit overgrowths	the sulphide part calculated for 100 per cent	ingrown sphalerite crystals
Zn	44,88%	48,45%	52,58%
Fe	14,71	15,87	11,51
Mn	1,01	1,09	1,19
Cu	0,37	0,39	0,53
S	31,68	34,20	32,72
CaO	2,43		
MgO	0,75		
CO <sub>2</sub>	2,72		
insol. residue	1,23		
	<hr/> 99,78%	<hr/> 100,00%	<hr/> 99,73%

Spectroscopically Cd could be detected in traces in the ingrown sphalerite crystals.

In our polished sections we detected in addition to these two sphalerites which are inspite of the divergence of their composition and appearance undoubtedly syngenetic, another very interesting sphalerite of younger origin. First we noticed a little tetrahedral crystal contained as inclusion in the pyrrhotite. On the basis of its reflection capacity as well as its internal reflexes it could be only assumed to be a sphalerite, however, on examination between crossed nicols the mineral showed marked dark bluish — dirty violetlike interference colours, thus behaving like an anisotrope. Subsequently we found in some of our polished sections this sphalerite overgrown on pyrite crystals or older isotrop sphalerite granules, or ingrown in siderite as radial needles forming crystal groups resembling the „Schalenblende” entities (microphoto 13.). In crystalgroups of the sphalerite, formed from acid solutions in the course of the later ore forming phase and pseudomorph after wurtzite, overgrown on the older sphalerite is became immediately conspicuous that the colour of our mineral was somewhat darker (more bluish) than that of



the older sphalerite. Owing to its crystal needles being appreciably thinner than the granules of sphalerite its internal reflexes were far more numerous and showed a lighter colour. In each sample the anisotropic behaviour is striking. Ramdohr mentions that sphalerites containing a copious amount of iron might be anizotrope, however, it is open to question why only the crystals of this younger generation are anizotrope. Owing to the minute size of the needle aggregates and their small number this sphalerite could not be analysed. It should still be mentioned that in this anizotrope sphalerite chalcopyrite inclusion could not be detected.



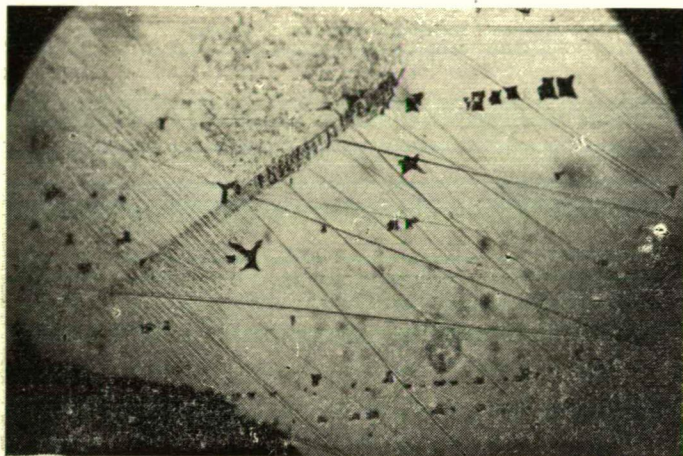
13.

Acicular radiated crystal group of secondary, anisotrope sphalerite. Oel imm. 400  $\times$ , N ||

### Chalcopyrite

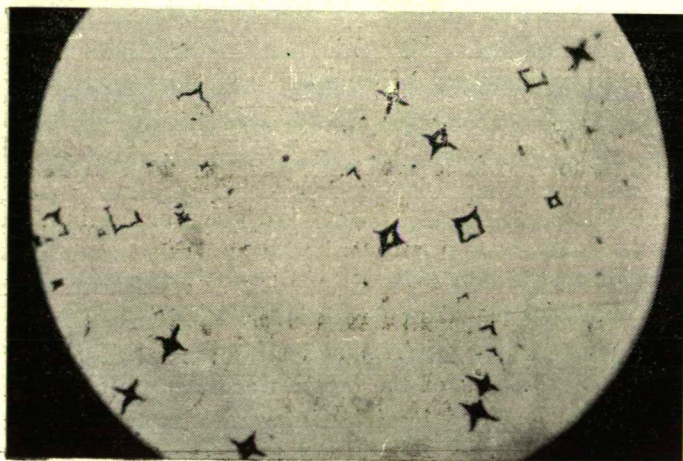
Chalcopyrite is the fourth member of the older ore formation. Quantitatively it is far less significant than pyrrhotite and sphalerite. In the samples collected in the waste tip of Alsórózsabánya it was crystallized and associated with arsenopyrite as overgrowths on rock lodes. The crystals are pseudotetrahedrons 5—6 mm in size, forms  $(111)$  and  $(\bar{1}\bar{1}\bar{1})$  developed approximately to the same extent. The surfaces of the crystals are coated by orientedly overgrown sphalerite. Sphalerite plates  $(111)$  intergrew hypoparallel according to this plane planes  $(\bar{1}\bar{1}\bar{1})$  were composed of numerous minute crystals. On examining them in polished sections it could be observed that the chalcopyrite crystals contained many strongly corroded pyrite granules and were crowded at certain points with sphalerite „stars” migrating from the border, the sphalerite cortex, towards the interior, whereas sphalerite contained the granular lamellar chalcopyrite remnants as shown on microphoto 14. Thus the two syngenetic ores mutually replace each other at the border of the chalcopyrite crystals.

The always xenomorphous granules of the massive chalcopyrite show a fine twin-lamellar structure and in each granule the sphalerite stars characteristic of chalcopyrites formed at high temperature, also mentioned by Pantó<sup>3</sup> from this provenance can be detected. Some granules showed a whole



14.

Chalcopyrite with sphalerite «stars» migrating into its interior. Oel imm. 500  $\times$ , N  $\parallel$



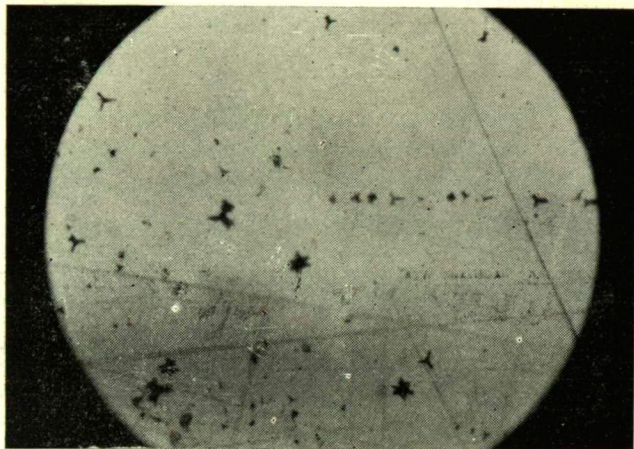
15.

Sphalerite stars in chalcopyrite. Oel imm. 600  $\times$ , N  $\parallel$

star collection (microphoto 15.). The size of the stars ranges from a few microns to a size hardly visualable at 1200 magnification. Their shape varies too. Usually, the polished sections are perpendicular to the diagonal axis, the stars have four branches. Less frequently the stars are perpendicular to the trigonal axis in the polished sections, they have three and in the case of twins-

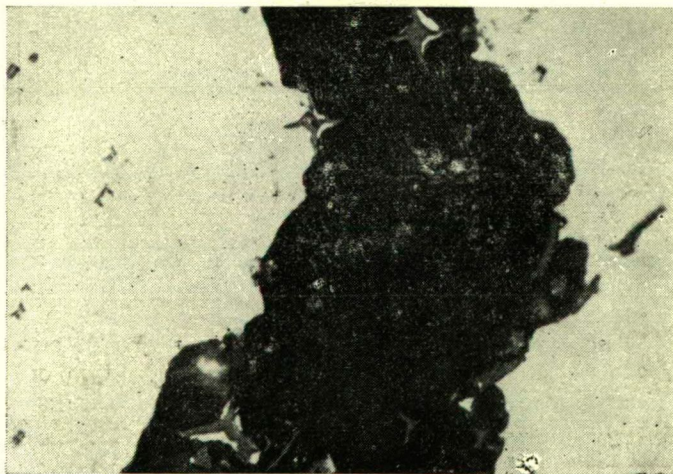


six branches (microphoto 16.). Part of the stars are composed of pure sphalerite, in others in the middle of the sphalerite star a to a greater or lesser extent replaced chalcopryite nucleus can be detected. In some chalcopryite crystal granules the sphalerite stars extend along the chalco-



16.

Sphalerite stars, the section is perpendicular to the axis of trigonal. Oel imm.  $500\times$  N ||



17.

Sphalerite stars in siderite replacing chalcopryite with rests of the latter. Oel imm.  $800\times$  N ||

pyrite twin lamellae in straight parallel rows. If siderite replaces chalcopryite on the borders of the sphalerite stars a small amount of chalcopryite can still be found as sphalerite is more difficultly replaced than chalcopryite (microphoto 17.).



Helke<sup>7</sup> found similar stars in the chalcopyrite of Kisbánya (Roumania), whereas the present writers detected some in the chalcopyrite of Oradna (Roumania), however, in no place were they so abundant and various as in Nagybörzsöny. An interesting phenomenon was the detection of a chalcopyrite dismixture in the sphalerite crystals surrounded by chalcopyrite, whilst chalcopyrite — on the other hand — contained sphalerite stars. This structure supports convincingly the assumption that the two ores formed syngenetically at very high temperature. Our chalcopyrites contain, in addition to the stars, numerous somewhat larger, rounded, droplike, or irregularly outlined sphalerite inclusions 25—35 micron in size, apparently also the products of dismixture. In our polished sections sphalerite is in many places replaced by siderite. The sphalerite replaced by siderite assumes sometimes the shape of a star in the replacing carbonate (microphoto 18.). These „stars”



18.

Sphalerite «stars» forming by means of resorption  
in the replacing siderite. Oel imm. 400 $\times$ , N II

are identical formations to those observed in the chalcopyrite and mentioned above with respect to the orientedly intergrown chalcopyrite-sphalerite system. In both cases the „stars” are products of resorption which, in spite of their resemblance to the crystal germs due to dismixture, are of exactly opposite origin as they form at the dissolution of sphalerite. In two our sections in addition to chalcopyrite the minute granules of chalcocite surrounded by covellite platelets could also be detected.

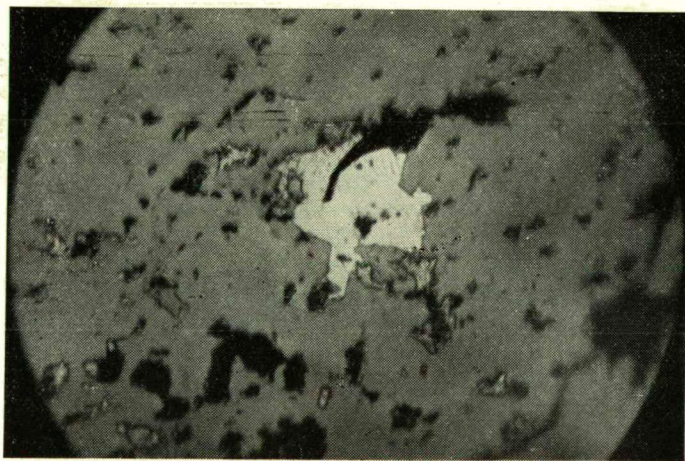
#### Bismuth ores, native gold

G. Pantó collected several interesting samples of the material of the new exploitations in the surroundings of the pit of Rózsabánya. He examined them and gave us some for our investigations. It could be established that the ore is arsenopyrite and that it is very like the glaukodote termed „allocklase” which can be found in the white limestone of Erzsébetbánya in Oravicabánya (Roumania) and which also contains bismuth. Similarly to glaukodote the arsenopyrite from Rózsabánya is also impregnated in a spongelike manner with



patches varying in size and containing bismuth minerals. Our polished sections contain besides bismuth minerals younger than arsenopyrite also older pyrite and chalcopyrite which are replaced by arsenopyrite. The chalcopyrite is crowded with sphalerite stars. The bismuth ores replacing chalcopyrite, in the first place bismuthinite, absorb the latter and accumulate the less soluble sphalerite remnants at the border of the two ores.

Among the bismuth minerals filling out the pores of arsenopyrite and thus replacing it, native bismuth is the oldest. Its amount is significant, the granules are rounded, droplike and beside the white arsenopyrite they seem to have a reddish colour, the characteristic twin lamellae very visible on them. In the analysed sample the amount of native bismuth was 11 per cent. Apart from bismuth, bismuthinite is the most frequent bismuth ore. Beside arsenopyrite bismuthinite has always a slightly bluish grey tint, its reflexion capacity is weak, the reflexion pleochroismus can be instantaneously observed, the interference colours are striking and depend upon the orientation. Its characteristic thin, columnar, muddled, aggregates can be found in the smaller hollows or on the border of arsenopyrite, in which case the minute, fine crystal needles are overgrown on its crystalline mass. Cosalite can be found in the vicinity of native bismuth replacing it. Beside arsenopyrite it seems to have a light greyish colour its reflexion capacity is weaker, it does not show any pleochroismus the interference colours are not bright. It has a granular structure. Microchemical examinations showed in addition to bismuth also lead. It may be that part of the silver is also bound to this ore.



18.

Native bismuth (light grey), native gold (white)  
in arsenopyrite (dark grey). Oel imm. 450  $\times$ , N II

In one of our polished sections a bismuthtelluride of the provenance, most probably tetradymite, could also be identified. Beside arsenopyrite its colour is light cream. It possesses the splendid cleavage surface characteristic minerals with a layer-lattice, as well as a strong reflexion capacity, its interference colours are identical with those of the tetradymite from Csiklova (Roumania). Tellur, detected in traces in the analysis, is also contained in it.

In addition to the bismuth minerals — through far less frequently — jamesonite can also be found in the hollows of arsenopyrite. The reflexion of its columnar crystal needles is weaker and a little more greyish than that of arsenopyrite and shows a light greenish tint. Reflexion pleochroismus is characteristic.

Beside the bismuth-ores, in the first place beside native bismuth, the irregular platelets of native gold, a few microns in size, could be detected (microphoto 19.). The lighter colour indicates its silver content. According to the analysis of Csajághy<sup>3</sup> the gold content was 204 gr/t, thus it occurs as free gold in this ore.

Analyses of this strange arsenopyrite ore, replaced by bismuth-ores, were made by Csajághy as well as by the present writers. The results are approximately corresponding (calculated for 100 per cent).

	Csajághy	Writers
Fe	23,62%	24,87%
Co	0,12	0,27
Zn	0,04	—
Pb	3,93	4,31
Cu	0,24	0,22
As	30,96	30,34
Bi	21,44	21,62
Sb	0,33	0,73
Te	—	trace
S	19,32	17,64
	100,00%	100,00%

(It is deemed of interest to mention that the bismuth content of the „alloclase” of Oravicabánya ranged between 22,96—32,83 per cent.)

The significant amount of iron is in first place the component of arsenopyrite, pyrite, chalcopyrite and jamesonite; cobalt is that of arsenopyrite, zinc that of sphalerite, which could not be detected in our polished sections; lead, that of cosalite and jamesonite; copper that of chalcopyrite; arsenic that of arsenopyrite; bismuth that of native bismuth, bismuthinite, cosalite and tetradymite-traces; tellur that of the latter; and finally antimony that of jamesonite.

Bismuthinite needles penetrate into the hollows of the samples overgrown on crystallized arsenopyrite. The aggregate of the extremely fine silky lustreous crystal aggregates of arsenolite coat the ores mentioned above. The arsenic they contained could be demonstrated by chemical analysis. Usually, thus also within the Carpathian mountain range, bismuth and its minerals, save for very rare bismuth tellurides, can only be found in hardly detectable traces in sulphide ore occurrences bound to volcanic rocks of the young Tertiär period (Recsk, Kapnikbánya, Felsőbánya, Kisbánya). The occurrence of this element and its minerals, foreign to the mineral-associations of this lode, produces a specific mixed lodetype characteristic for Nagyörzsöny.

#### Galena II. and lead—antimony ores

The occurrence of the galena II., more copious than that of galena I., is bound to the ore of the Fagyosasszony lode. It replaces pyrrhotite, sphalerite, chalcopyrite, the former often lamellarly. If it is associated with the harder ores it gets polished and is full of characteristic triangular cleavages. Along

its cleavage it gets cerussitized. The small amount of jamesonite and the very uncommon semseyite associated with it are formed from it. The irregularly intergrown needle aggregates of jamesonite extending centripetally from the border of the crystals and crystal aggregates of galena occurred more frequently. Among the needles crystal twins are very common. The reflexion pleochroismus is conspicuous as is beside the izotrope galena the anizotropy. The characteristic fanlike group of lamellar crystals of semseyite occurring far less frequently could merely be detected as crystal groups in two sections can be found embedded in the carbonate, coating the galena. It did not show reflexion pleochroismus, the whole crystal group was hardly one mm in size, however, between crossed nicols it showed the pinkishgreyish anizotropy characteristing the semseyite occurring in Kisbánya with which it was compared. Microchemically lead and antimony could be demonstrated in the semseyite granules. Apparently semseyite, of which alone in the mining district of Szatmár four provenances are known, occurs if also only scarcely, in other as yet unknown mining districts. Antimony could not be detected, the slight amount of antimony contained in the analysed ore samples is bound to these two lead-antimony-sulphides.

Of the few associated minerals barite, found in the lower adit, was interesting. Its crystals are thin and columnar, a few mm in size, they occur associated with pyrite and are partly coated by calcite, they extend in the direction of crystallographic axis *a* and only show lustreous curved platelets according to (011). Their terminal platelets are either covered by an entirely curved plate or they fray out. The fine crystalline quartz, having in the older generation apatite inclusions, furthermore the zonal structured dolomite, curved in a lentiform manner, sometimes showing a red colour, its crystals often being replaced by siderite and finally the white calcite overgrown  $-\frac{1}{2}R$  small crystals with curved planes on the walls of the little hollows, should still be mentioned.

### CONCLUSIONS

In the Carpathians there are still two other hydrothermal ore-occurrences bound to young volcanic rocks and formed at a similar high temperature as those of our mining districts: Oradna (Rodne-Veche, Roumania) and Kisbánya (Herja, Roumania) also mentioned by Pantó.

Pyrrhotite was the primarily dominating ore in all three provenances. Valleriite does not only occur in Kisbánya, but also in Nagybörzsöny. The sphalerite of all three provenances is strikingly rich in iron. The chalcoppyrite of all three provenances contains sphalerite stars. The principal ore minerals of all the three are the same:

Nagybörzsöny	Kisbánya (Herja)	Oradna (Rodna-Veche)
pyrrhotite sphalerite (15,87% Fe) chalcoppyrite arsenopyrite galena pyrite II.	pyrrhotite sphalerite (14,69% Fe) chalcoppyrite arsenopyrite galena pyrite II.	pyrrhotite sphalerite (14,27% Fe) chalcoppyrite arsenopyrite galena pyrite II.

The hydropyrite-melnikovite-pyrite II-marcasite-siderite formed from pyrrhotite are identical in Nagybörzsöny and Kisbánya. A common feature of



all three mining districts is that arsenopyrite occurs in an appreciable amount in their lodes. This fact is in contrast with the establishment of Helke, who states that arsenopyrite and arsenic ores in general are very rare in the ore lodes of North-Eastern Roumania and quite unknown in those of North Hungary.

It could be established that arsenopyrite occurs in larger amounts in Nagyörzsöny and Oradna (perhaps even also in Kisbánya) than do the antimony minerals which are usually far more common in hydrothermal ore deposits bound to the tertiary rocks of the Carpathians. Among three mining districts antimonite only occurs in Kisbánya. In Nagyörzsöny and Oradna lead-antimony-sulphides occur only rarely and in small amounts.

As regards bismuth ores Nagyörzsöny differs from the two other mining districts. In the galena of Kisbánya bismuth could only be detected in traces (0,001 per cent), probably it can also only be found in traces in Oradna. As contrasted with these traces the arsenopyrite of our mining district is permeated with bismuth and contains a strikingly large amount of this ore. Another feature in which Nagyörzsöny differs from the two others is that its arsenopyrites containing bismuth are also very rich in gold. In Kisbánya the average Au content of the ore is 0,5 g/t, in Oradna it is 0,3—0,2 g/t. The ores of these mining districts are not so rich in gold as are those of Nagyörzsöny (204 g/t). Finally the bismuth tellurides of Nagyörzsöny — known since a long time and now again observed, — and unknown in the other two mining districts, should still be mentioned. Consequently Nagyörzsöny is in every respect the sulphide mining district possessing the most interesting mineral — and element combination. Its element combination — compared with that of the two other mining districts dealt with — can be represented as follows:

Nagybörzsöny:	<u>S</u>	<u>O</u>	<u>Fe</u>	<u>Zn</u>	<u>Pb</u>	<u>Cu</u>	<u>Si</u>	<u>C</u>	<u>Ca</u>	<u>As</u>	<u>Hg</u>	<u>Mn</u>	
Kisbánya:	<u>S</u>	<u>O</u>	<u>Fe</u>	<u>Zn</u>	<u>Pb</u>	<u>Cu</u>	<u>Si</u>	<u>C</u>	<u>Ca</u>	<u>As</u>	<u>Hg</u>	<u>Mn</u>	
Oradna:	<u>S</u>	<u>O</u>	<u>Fe</u>	<u>Zn</u>	<u>Pb</u>	<u>Cu</u>	<u>Si</u>	<u>C</u>	<u>Ca</u>	<u>As</u>	<u>Hg</u>	<u>Mn</u>	
Nagybörzsöny:	<u>Sb</u>	<u>H</u>	<u>Ba</u>	<u>Ag</u>	<u>Bi</u>	<u>Co</u>	<u>F</u>	<u>P</u>	(Cd)	<u>Au</u>	(Ni)	(Te)	(Mo)
Kisbánya:	<u>Sb</u>	<u>H</u>	<u>Ba</u>	<u>Ag</u>	(Bi)	—	<u>F</u>	<u>P</u>	(Cd)	(Au)	(Ni)	—	—
Oradna:	<u>Sb</u>	<u>H</u>	<u>Ba</u>	<u>Ag</u>	—	—	<u>F</u>	<u>P</u>	(Cd)	(Au)	—	—	—

The dominating elements of the mining districts are under lined, the more frequent ones and those which can be demonstrated analytically, dotted whereas the quite rare minor elements which can only be observed spectroscopically are in brackets.

The element association of the three mining districts is also identical, with the exception that bismuth, occurring in significant quantities in Nagyörzsöny and tellure and cobalt detected in traces, cannot be found in the ores of the other two mining districts.

Within the Carpathians range of mountains three hydrothermal occurrences furnish ore containing iron in abundance. They are bound to young tertiary rocks and formed at the highest temperature.

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## ИСКОПАЕМЫЕ МЕСТОРОЖДЕНИЯ СЕРНИСТОЙ РУДЫ В НАДЬБЭРЖЕНЬ.

— ШАНДОР КОХ И ЮЛИЙ ГРАССЕЛЛИ —

Хотя в настоящее время в Надьбэржень идёт только разведочная работа, но по обнаруженным ископаемым уже можно установить, что он является самым богатым ископаемыми рудным месторождением Родины, зарождённым при высшей температуре. Рудами и аксессуарными минералами его являются:

самые старые минералы — апатит, кварц, пирит I, галенит I, пирротин, валлериит, сфалерит I. (пирротин и халкопирит, с размешиванием), халкопирит (сфалеритными звёздочками);

более молодые минералы,  
отчасти из материала

более старых — арсенопирит, тетраэдрит, висмут, висмутин, золото, галенит II, косамит, сфалерит II, джемсонит, семсеит, тетрадимит, чикловаит, гессит, педзит, аргентит, прустит, молибденит, барит, доламит, калцит;

минералы зоны окисления — гидропирит — мелниковитпирит — пирит II, марказит, сидерит, магнезит, кронштейтит, халкозин, ковеллин, игольчатый железняк, лимонит, арсенит.

Минеральный агрегат его очень близкий к агрегатам месторождений Геря и Родна-Веке в Румынии, но отличается от этих своими висмутовыми минералами и его арсенопирит — своим содержанием золота.





## DATA ON THE OXIDATION OF SULPHIDE-ORE DEPOSITES

By S. KOCH and Gy. GRASSELLY

Our investigations published last year dealt in general with the dissolution and oxidation — resulting from the action of sulphuric acidic solutions — of some significant sulphide ores such as galena, sphalerite, pyrite, tetrahedrite, as well as ore mixtures consisting of these ores and their mixtures with pyrrhotite. In the course of the examinations the change in the free sulphuric acid and total sulphate content, the change in the pH and conductivity, as well as that of the metal content were measured. On the basis these measurements a distinct correlation could be established between the change relating to the factors mentioned above and those concerning the dissolution and oxidation of the different ores and ore mixtures. It should be established that the environment exerts a very strong influence on the dissolution of the various ores, as well as the difference in potential existing between the respective ore and other neighbouring ore granules. The extent of the change is well reflected by the aforementioned changes the measuring of which can be effected in a relatively short time.

In the following the continuation of our work of last year in the sense described then is contemplated i. e. that the study of the dissolution and oxidation conditions of the ore debris corresponding to the mineral association characterising an individual mining district is the chief purpose, notwithstanding that the dissolution conditions in general must also be dealt with, as the dissolution and oxidation conditions of the different ores are strongly influenced by their environment and impurities, more precisely they are determined by them. For this reason the mineral association of Recsk was investigated first. Simultaneously we attempted to establish to what an extent the copper sulphate and ferric sulphate content of the solutions sickering over the ores influences their dissolution. Selected „pure” enargite, as well as a mixture of enargite-pyrite was treated with a solution of 0,05 N sulphuric acid containing copper and ferric sulphate respectively, as well as with one of 0,05 N sulphuric acid and similarly to last year the changes occurring in the solution were examined. A separate sample was selected to observe the dissolution conditions of the pyrite of Recsk, it was treated with a pure sulphuric acid solutions of the concentration mentioned above. The apparatus described in our previous communication was used and the course of the examination was identical too.

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Appeared in Magyar Tudományos Akadémia Műszaki Tudományos Osztályának Közleményei (Publications of the Technical Department of the Hungarian Academy of Science) Vol. VIII.

The tests were as follows:

Composition of the test:

1. Pure selected enargite
2. Pure selected enargite
3. Pure selected enargite
4. Ore mixture (enargite-pyrite)
5. Ore mixture (enargite-pyrite)
6. Ore mixture (enargite-pyrite)
7. Pure selected pyrite

Composition of the circulating solution:

- about 0,05 N sulphuric acid.  
 about 0,05 N sulphuric acid + ferric sulphate. Iron content of the starting solution 0,2236 g/l Fe.  
 about 0,05 N sulphuric acid + copper sulphate. Copper content of the starting solution 0,2847 g/l Cu.  
 Like solution 1.  
 Like solution 2. Iron content of the starting solution 0,2348 g/l Fe.  
 Like solution 3. Copper content of starting solution 0,2782 g/l Cu.  
 Like solution 1.

The change of the amounts of free sulphuric acid, total sulphate, iron, copper and arsenic contained in the solutions was examined. The results are illustrated in the following tables: (In the period between the taking of the first and the last sample the same 5 liters sicker twelve times over the ores, the amount merely decreasing through the sampling.)

Table 1.

*The change of total sulphate (a), free sulphuric acid (b) and bound sulphate (c) contained in the solutions in  $SO_4$  g/l:*

Solution	at the beginning	at the end	change in the course
	of the examination		
1. a	2,158	2,286	+ 0,128
b	2,158	2,104	- 0,054
c	0,000	0,182	+ 0,182
2.	3,090	3,185	+ 0,095
	2,518	1,948	- 0,570
	0,572	1,237	+ 0,665
3.	2,678	2,891	+ 0,213
	2,248	1,819	- 0,429
	0,430	1,072	+ 0,642
4.	1,933	2,396	+ 0,463
	1,933	1,952	+ 0,019
	0,000	0,444	+ 0,444
5.	3,010	3,294	+ 0,284
	2,405	1,729	- 0,676
	0,605	1,565	+ 0,960
6.	2,668	2,942	+ 0,274
	2,248	1,886	- 0,362
	0,420	1,056	+ 0,636
7.	2,068	2,299	+ 0,231
	2,068	1,862	- 0,206
	0,000	0,437	+ 0,437



Table 2.  
The change of the iron- copper- and arsenic content  
of the solutions in g/l:

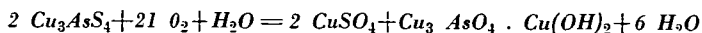
Solution		at the beginning	at the end	change in the course
		of the examination		
1.	Fe	0	0,0091	0,0091
	Cu	0	0,0198	0,0198
	As	0	0 0035	0,0035
2.	Fe	0,2236	0 2348	0,0112
	Cu	0	0,0039	0,0039
	As	0	0,0020	0,0020
3.	Fe	0	0,0548	0,0548
	Cu	0,2847	0,3089	0 0242
	As	0	0 0100	0 0100
4.	Fe	0	0,0891	0,0891
	Cu	0	0,0094	0,0094
	As	0	0 0025	0,0025
5.	Fe	0 2348	0,2815	0,0467
	Cu	0	0,0145	0,0145
	As	0	0,0030	0,0030
6.	Fe	0	0,0822	0,0822
	Cu	0,2782	0,3242	0,0460
	As	0	0,0045	0 0045
7.	Fe	0	0,0572	0,0572
	Cu	0	0,0090	0,0090
	As	0	0,0015	0,0015

In the course of the investigations carried out in 1952 in most cases merely the free sulphuric acid content diminished, however, the total sulphate content remained unchanged. On the other hand, in the solutions circulating over the pyrite-enargite mixture the total sulphate content increased significantly, to a greater extent than in the solutions circulating over the pure pyrite or pure enargite. Indicating that in cases when the pyrite and enargite are in contact, the oxidation is more intense than in the case of pure ores in spite of the difference in potential being slight between the two ores. The pyrite-enargite mixture underwent the most intensive oxidation in pure N sulphuric acid (0,05), inasmuch as not only the total sulphate content increased to the greatest extent, but even the amount of the free sulphuric acid contained in the solution increased.

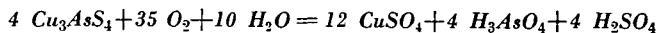
Pyrite dissolves and oxidizes to a greater extent in a solution of pure sulphuric acid than enargite. Based on the results of the previous and present investigations the following sequel can be established according to the decrease in solubility: tetrahedrite, sphalerite, galena, pyrite, enargite, chalcopryrite.

These results are in good agreement with the results reported by Nishihara regarding his investigations carried out in ferric sulphateous solutions.

It can be assumed that the oxidation of enargite takes place according to the following equation:



Accordingly basic copper arsenates forms. However, they decompose on the action of sulphuric acid and if the latter is not bound in some way, arsenates do not form, but the enargite containing copper dissolves totally and in addition to copper sulphate and free sulphuric acid  $\text{H}_3 \text{ AsO}_4$  also forms. Thus in this case the oxidation of enargite can be represented as follows:



This explains the increase of the amount of the total sulphate and free sulphuric acid contained in the pure sulphuric acid solution circulating over the pyrite-enargite mixture. The change of the total sulphate content expresses the extent of the oxidation as the total sulphate content of the solution only increases if the sulphide contained in the ores is oxidized to sulphate.

The change of order of magnitude of the arsenic content is nearly identical to that of the copper content. The amount of copper and arsenic contained in the solutions shows the greatest increase both in ores and ore mixtures if they are exposed to the action of solutions containing copper sulphate. In solutions containing copper sulphate the change of the iron content is also more significant than in solutions containing ferric sulphate.

Our present investigations support also the results obtained in 1952, inasmuch as in the case of the mixtures — although there is a small potential difference between pyrite and enargite — the increase of the total sulphate content (the oxidation of the ore) exceeds appreciably the change of the total sulphate amount measured in the solutions circulating over the pure enargites.

In pure sulphuric acid solutions the pyrite decomposition sets in initially as indicated by the high iron content observed in solution No. 4, as well as by the fact that the iron content of the pure, selected solutions circulating over the enargites, containing at the most quite slight pyrite impurities also increases considerably in a relatively short time. On the action of the evolved ferric sulphate and sulphuric acid in the presence of air the oxidation of the enargite starts and becomes always more intensive as the concentration of the copper sulphate and sulphuric acid increases, and if the sulphuric acid forming in the course of the decomposition is not bound in some way, the enargite is oxidized to copper sulphate and arsenic acid under formation of sulphuric acid. The experiments show that indeed copper sulphate exerts a more intensive action than ferric sulphate. If the sulphuric acid concentration diminishes significantly it paves the way for the formation of different copper arsenates. Taking the mineral association of Recsk into consideration it seems probable that the oxidation takes place as described above.

The results reported in our previous paper point to the fact that for the interpretation of the dissolution and oxidation conditions of the different ores and ore mixtures (their combination corresponding to the different mineral associations) the changes of the sulphuric acid and sulphate content, as well as those of the pH, conductivity and those of the amount of the contained metal, do not offer a suitable explanation, hence the observed phenomena cannot be solely due to the changes described above. For instance there



is no explanation for the change of the ferrous-ferric ratio, as well as for the fact that e. g. not the slightest iron hydroxide separation could be detected in the solution circulating on the tetrahedrite the pH of which was 2,40 and its free sulphuric acid content 0,78 g  $\text{H}_2\text{SO}_4/\text{l}$ ; whereas in a solution circulating on an ore mixture of galena-chalcopryrite-pyrrhotite the pH of which was 2,00, containing 1,760 g  $\text{H}_2\text{SO}_4/\text{l}$ , or in a solution of pH 2,20 containing 1,331 g  $\text{H}_2\text{SO}_4/\text{l}$  of free sulphuric acid circulating over a tetrahedrite-pyrite mixture, an intensive iron hydroxide separation could be observed.

The redoxypotential on the other hand, also provides an adequate explanation for these phenomena. Goldschmidt was the first to use the term oxidation potential in geochemistry, recently Scserbina, Mason, Chapman, and Schweitzer also use it. The dissolution, transport and separation respectively, of elements occurring in different oxidation forms are greatly influenced by the oxidation potential of the environment, i. e. the latter determines it.

The potential of a system is the more negative the higher the concentration of the ions of lower valency compared with those of higher valency and on the other hand, the more negative the normal potential, the more vigorously the system reduces, whereas the more positive the potential of a system the more vigorously it oxidizes in the case of identical concentrations. Hence every system exerts a reducing influence on the systems having a more positive redoxypotential and vice versa.

In the course of our previous investigations we observed that a tetrahedrite solution mainly contained iron as ferrous iron and that in the course of the circulation the ferrous content of the solution increased intensely, or that e. g. in a solution of tetrahedrite-chalcopryrite-pyrrhotite the ferrous content also showed a rise, whereas in other cases as for example a solution of galena or sphalerite or even in that of pyrite the increase of the ferrous iron content was very slight even decreasing in some places in spite of the fact that in the course of the dissolution it dissolved first as ferrous iron. Thus in the case of the latter ores the oxidation was more intense than in that of the former ones. In the course of the experiment the quantity of the dissolved metals was also determined. As among these metals in the case of iron, copper and manganese the valences vary, it is obvious that in the first place the action exerted by copper and manganese on the change of the ferrous-ferric ratio had to be examined.

The potential of  $\text{Fe}^{+2} = \text{Fe}^{+3} + e$  is 0,77 V, that of  $\text{Mn}^{+2} = \text{Mn}^{+3} + e$  1,57 V and that of  $\text{Cu}^{+1} = \text{Cu}^{+2} + e$  0,18 V. The values represent the normal oxidation potential, i. e. when the oxidized and reduced forms are present in equal concentration. This value is influenced by the change of concentration. For instance the normal potential of  $\text{Fe}^{+2}/\text{Fe}^{+3}$  is 0,77, if the  $\text{Fe}^{+3}/\text{Fe}^{+2}$  ratio is 100/1 the oxidation potential is 0,89 V, if on the other hand the  $\text{Fe}^{+3}/\text{Fe}^{+2}$  ratio is 1/100 then it will be 0,65 V.

In the range of a certain pH the latter does not influence the oxidation potential. Thus for instance the oxidation potential of  $\text{Mn}^{+2}/\text{Mn}^{+3}$  remains constant till pH 4, in an acid medium the oxidation potential of  $\text{Fe}^{+2}/\text{Fe}^{+3}$  is 0,77 V, as the pH increases and attains a certain value, approximately at pH 2—3, the oxidation potential suddenly decreases and the separation of the ferric hydroxide sets in. We also observed that at the decomposition of sulphide ores — like at that of the silicates and carbonates — the iron and manganese occurring primarily associated separate in the course of the decom-

position the iron separating out first in the form of hydroxide. This phenomenon can also be accounted for by the variations of the oxidation potentials.

Of the three systems involved the  $\text{Cu}^{+1}/\text{Cu}^{+2}$  system has the lowest, the  $\text{Fe}^{+2}/\text{Fe}^{+3}$  the mean, and the  $\text{Mn}^{+2}/\text{Mn}^{+3}$  the highest potential. The influence exerted by copper sulphate and manganese sulphate on the oxidation of ferrous iron to ferric iron in a 0,05 N sulphuric acid solution was examined, as well as the rate of the ferrous oxidation if copper sulphate and manganese sulphate are simultaneously present. Hence the change of the ferrous content was systematically measured in sulphuric acid solutions the composition of which corresponded to that described above.

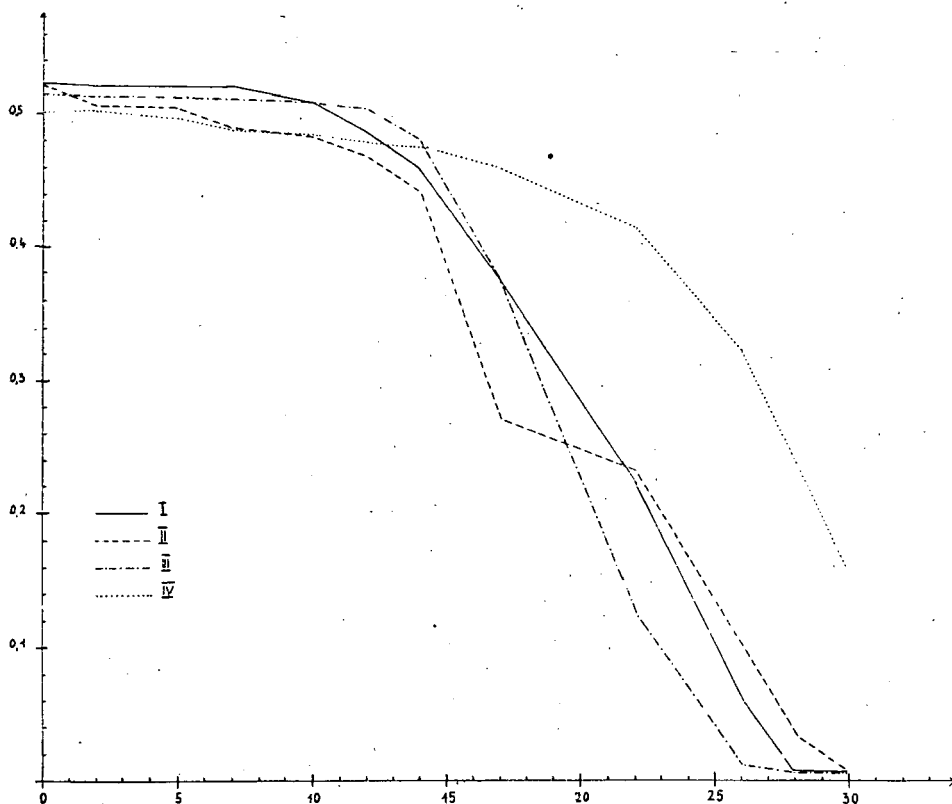
Solution No. I. contained only ferrous sulphate, the iron content of the solution at the start was 0,522 g Fe/l. Solution No. II. contained the same amount of iron and 0,273 g/l copper as copper sulphate. Solution No. III. contained 0,514 g/l ferrous iron and 0,184 g/l manganese as mangano-sulphate. Finally the ferrous iron content of the solution No. IV. was 0,502 g/l and contained the same quantity of copper and manganese as in the case of solutions III., IV. respectively. The sulphuric acid concentration of the solutions was about 0,05 N.

Table 3.  
The change of the ferrous iron content in g/l :

The data according to the days after the examinations were started	I	II	III	IV
	solutions			
0	0,522	0,522	0,514	0,502
2	0,520	0,506	0,512	0,502
5	0,520	0,504	0,512	0,496
7	0,520	0,490	0,510	0,488
10	0,508	0,482	0,508	0,484
12	0,486	0,468	0,504	0,478
14	0,458	0,442	0,480	0,474
17	0,374	0,272	0,376	0,458
22	0,224	0,232	0,126	0,414
26	0,060	0,100	0,012	0,322
28	0,006	0,034	0,006	0,240
30	0,006	0,006	0,006	0,164
60	0,003	0,006	0,003	0,006

On the basis of the above considerations, as was anticipated, the rate of the oxidation of ferrous iron was slower in copper sulphateous solution and more rapid in manganese sulphateous solutions, as compared with the oxidation of the ferrous iron contained in pure sulphuric acid ferrous sulphate. On the other hand, in the solution where the starting solution contained manganese sulphate and copper sulphate simultaneously the oxidation-reduction processes run down in the first place between the lowest and highest potential system. Thus owing to the action of the oxidation potential the simultaneous presence of manganese and copper retards the oxidation of ferrous iron. This assumption, as well as the significance of the influence of the oxidation potential on the different processes is supported by the establishment made in the course of our previous examinations that the ferrous iron content of the solutions circulating over the tetrahedrite ore debries — containing at the end of the experiment-series 0,045 g/l — manganese and 0,071

g/l copper was permanently dominating, the amount of the ferrous content exceeding manifold that of ferric iron.



On the other hand, in the case of sphalerite or galena the solutions circulating over them contained only manganese, but no copper, thus the manganese accelerated the oxidation of the ferrous iron and ferric iron dominated in the solutions.

It is contemplated to investigate the significance and role of the oxidation potential under conditions in which a solution is also in contact with a solid phase.

## ОКИСЛЕНИЕ ПДАСТОВ СЕРНИСТЫХ РУД.

— ШАНДОР КОХ И ЮЛИЙ ГРАССЕЛЛИ —

Продолжая прошлогодние исследования по растворению и окислению рудной мелочи-чистого пирита, чистого энаргита или смеси пирита-энаргита, соответствующему составу минерального агрегата месторождения Речка, устанавливалось, что прежде начинается разложение пирита, а потом, по воздействию образованного сульфата железа и серной кислоты, начинается и окисление энаргита. Последний процесс становится всё сильнее по мере действия возрастающей концентрации сульфата меди и серной кислоты и если образованная выветриванием серная кислота каким-либо путём не связывается, то энаргит окисляется в сульфат меди и в мышьяковую кислоту с образованием серной



кислоты, однако, при этом основные клиноклазиты не образуются. Раствор, содержащий сульфат меди, действует более растворительно на минеральный агрегат вышеуказанного состава, чем раствор, содержащий сульфат железа.

На оксидацию содержания двухвалентного железа растворов, из металлов переменной валентности, оказывают сильное воздействие медь и марганец. Совместное присутствие меди и марганца замедляет оксидацию двухвалентного железа в значительной мере, вследствие различий в окислительно-восстановительных потенциалах отдельных систем.

## INVESTIGATION OF THE DISSOLVED AND FLOATING MATERIAL OF THE TISZA AND MAROS

By J. MEZŐSI and É. DONÁTH

The investigations were begun in 1951 and continued in 1952.

The quantity and quality of the dissolved salts, the amount of the floating material and its distribution according to the size of the granules were determined.

Every week water samples were taken from three different places. (Fig. 1.) From the Tisza in the vicinity of the ferry at Tápé, a little higher than the mouth of the Maros and at Szeged in the neighbourhood of the Boszorkánysziget about 5 km below the mouth of the Maros, where could be assumed that the two rivers mix completely, and finally from the Maros, approximately three and a half km from Deszk.

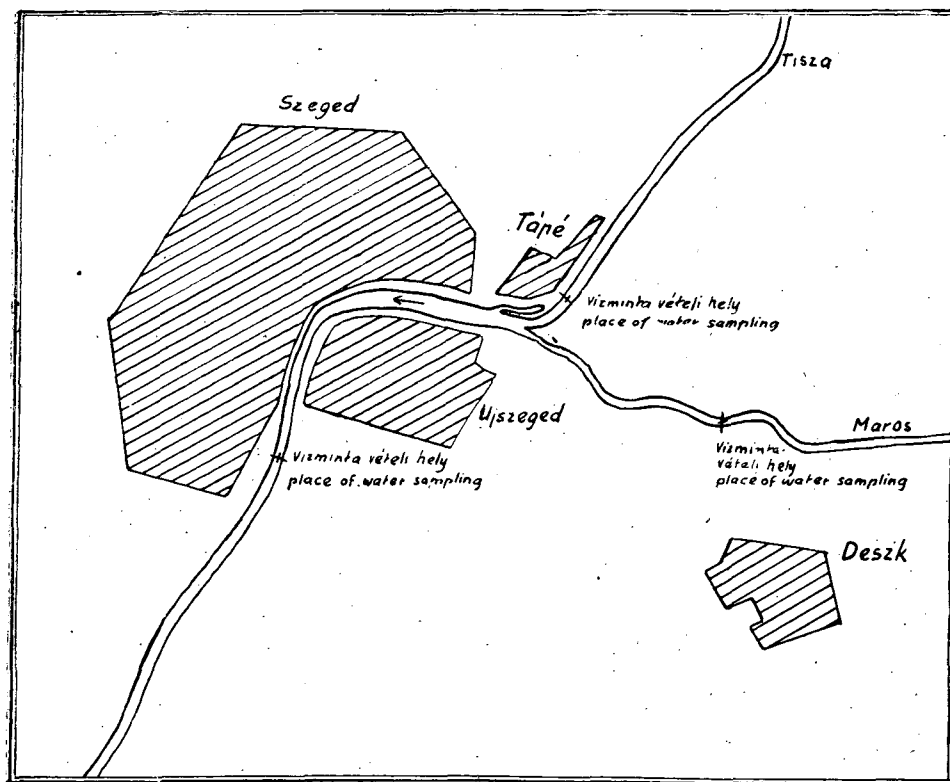


Fig. 1.

Delivered as a lecture to the Geochemical Commission of the Hungarian Academy of Science at its Meeting in February 1953. Appeared in Magyar Tudományos Akadémia Műszaki Tudományok Osztályának Közleményei (Publications of the Technical Department of the Hungarian Academy of Science) Vol. VIII.

During April the samples were only taken at Szeged, as then the Tisza owing to the high water level emerges from her bed and joins the Maros at a section above the mouth. In the second half of April the water level of the Maros was relatively low resulting in the surplus water of the Tisza damming the Maros which influenced the composition of the salts dissolved in its water to such an extent that the result of the analysis of the water sample taken on April 24th at Deszk corresponded almost completely with that taken from the Tisza at Szeged.

	Maros (Deszk) April 24	Tisza (Szeged) April 21
calcium ion	32,95 mg/l	32,07 mg/l
sodium ion	10,32	9,79
potassium ion	3,02	3,10
iron ion	0,26	0,26
hydrocarbonate ion	100,22	99,45
total oxide	6,40	6,10
alkalinity	1,64°	1,63°

The sampling was performed by the Branch of the Hungarian Hydrographical Institute at Szeged. At every sampling one liter of water was taken along the current from ten different depths, the obtained 10 liter of water were sedimented. This material was, as in the case of our previous investigation (1951), separated into clayey, muddy and sandy fractions. The water used for the chemical analysis was filtered through qualitative filter paper. Once a month at each sampling place the amount of the free oxygen and free carbon dioxide absorbed in the water was determined.

Considering that from the geochemical point of view only results based on systematic investigations can be used, the following facts were already taken into consideration from the beginning:

1. The sodium- and potassium ions, the calcium- and magnesium ions, as the carbonate and hydrocarbonate ions were separately determined. Furthermore, the sulphate- and phosphate ions, the iron- and chloride ions, all the dissolved salt, the total oxide, the silica, the undissolved residue, all the organic substances, the free oxygen and free carbon dioxide content of the water were also determined, as well as the alkalinity and the degree of hardness. Considering its minimum amount the manganese ion was estimated qualitatively once a month. Spectrographic examination of the trace elements was carried out by Mrs. M. Földváry to whom we are very grateful for her kind cooperation.

2. In each case the water samples were taken along the current of the Tisza and Maros respectively, at the site where the water mixed the best. Thus as regards both the floating and dissolved salts the most characteristic data of the rivers were obtained.

3. Considering that in the case of the Tisza the given water level always relates to Szeged and that of the Maros to Makó the amount of water flowing down can be calculated and thus a conclusion concerning the total quantity of the dissolved and floating material of the rivers reached.

The qualitative results of the investigations relating to the dissolved salt substance of the Tisza and Maros are illustrated on the graphs of Fig. 2. (see Tables 1—6.)



The quantity and quality of the total dissolved salt varies very much periodically, thus it can only be examined as a function of the water level. Concerning the quantitative changes the previous establishments that in the case of a high water level the amount of dissolved salts is smaller and in that of low water level higher, i. e. that the concentration increases, is valid. It showed a maximum at low water level on October 3rd. 0,44 g/l and a minimum in winter when the water is unusually high on December 1st. 0,13 g/l.

Total oxide ( $R_2O_3$ ). Under this term the total iron, manganese, aluminum, titane and phosphate amounts are summarised. They were approximately identical in both rivers. Between spring and autumn a gradual decrease could be observed. Considering that the total oxide group involves in addition to aluminum also iron, manganese, titane and phosphate this enables the drawing of conclusions as to the amount of the aluminum oxide. The mean value of the total oxide in the Maros at high water level is 6,5 mg/l subtracting the values of 0,23 mg/l of  $Fe_2O_3$  and 0,12 mg/l of  $P_2O_5$  (manganese occurred only rarely in traces and titane not at all) the amount of aluminum was 6,15 mg/l. In the Tisza at Tápé at high water level on the same basis the amount of the aluminum was 5,4 mg/l. At low water level in the Maros the total oxide amount is 2,83 mg/l, of this  $Al_2O_3$  is 2,58 mg/l. In the Tisza at Tápé the total oxide amounts to 3,45 mg/l ( $Al_2O_3$  3,31 mg/l).

The calcium ion can be ranged among the most sensitive ions as regards the fluctuations of the water level. It changes with nearly every fluctuation of the water level. It changes with nearly every fluctuation of the tide. At low water level the calcium ion content of the Maros was usually were only carried out systematically at Szeged, the calcium ion content was 55,6 mg/l on September 1st and at Szeged 58,7 mg/l on September 10th. In the course of April when owing to the high water level the measurings were only carried out systematically at Szeged, the calcium ion content was throughout approximately the same 30 mg/l. At high water levels the minimum in the Tisza at Tápé was 26,70 mg/l on November 26th, at Szeged 24,58 mg/l on November 19th and in the Maros at Deszk 27,65 mg/l on March 28th.

The quantitative fluctuations of the magnesium ion are relatively insignificant and a quantitative change corresponding to the water level could not be demonstrated. In both rivers the values obtained were approximately the same. The mean value was at high water level in the Tisza at Tápé 8,28 mg/l, at Szeged 7,04 mg/l, in the Maros at Deszk 8,32 mg/l. At low water level it was in the Tisza at Tápé 8,28 mg/l, at Szeged 8,16 mg/l, in the Maros at Deszk 8,20 mg/l.

The quantity of the sodium ion was the whole year round, — with the exception of a few cases — both at high and low water levels always greater in the Maros than in the Tisza. At low water levels with the increase of the dissolved salt concentration the sodium ion content rose too. In the Maros high values were obtained at low water level, e. g. on October 3rd 47,8 mg/l, on October 17th 49,4 mg/l. The influence exercised by the Maros on the Tisza at Szeged was well visible, inasmuch as the sodium ion content ranged almost always between that of the values of Tápé and the Maros. A maximum was measured on September 10th (35,58 mg/l) and at Tápé the maximum value was 32,35 mg/l on September 8th.

The change of the potassium ion was in proportion to that of the sodium ion, its quantity remaining, however, well below the value of the

latter. In the Maros it increased quantitatively particularly during the summer and autumn, the maximum also fell into this period it amounted to 6,25 mg/l on September 5th and 6,65 mg/l on October 10th. In the same period it was at Tápé 3,76 mg/l on September 8th and 2,71 mg/l on October 6th. The fluctuations of the potassium ion ranged in both rivers between low limits throughout the year, save for a few extreme cases, it varied between 2—4 mg/l.

The amount of the iron ion increased with the rising of the tide, at lower water levels it was lower, both rivers contained it in about the same quantity. The mean value was at low water level 0,09—0,11 mg/l, at high water level 0,16—0,21 mg/l. At high water levels in winter its amount increased to a great extent in the Tisza at Tápé, e. g. on December 30th it was 0,46 mg/l.

The manganese ion were always only present, in very small amounts, qualitatively they could only rarely be detected, this minimum amount also being mostly a characteristic feature of high water levels.

The amount of chloride ion in the Maros was generally the double of that found in the Tisza at Tápé. In March high values were obtained when the tide of the Maros flowed down, as well as after the flowing down of the summer tide when the maximum was attained on July 18th 79,50 mg/l and on March 21st 68,10 mg/l. After the flowing down of the tide the chloride ion content of the water of the river decreased in both cases. In the course of the summer months the diminished quantity rose again gradually, as the concentration increased. In samples taken from the Tisza at Tápé, with the exception of two cases, the chloride ion content was usually low, 10—20 mg/l. At Szeged the chloride ion content was owing to the greater amount of sodium chloride contained in the Maros, always higher than in the Tisza at Tápé.

The amount of the hydrocarbonate ion corresponds to the change in the quantity of the calcium ion. At high water levels it was low, at low water levels it was higher in both rivers. The whole year round it was less in the Tisza than in the Maros. These values ran parallel depending on the water level. In the beginning of the summer and the course of it the amount of the hydrocarbonate ion increased gradually. It reached its maximum at the end of August and beginning of September, in the Tisza at Tápé on September 8th it was 201,30 mg/l, in the Maros on September 5th, 181,17 mg/l.

The carbonate ion could be already detected in the Maros, as well as in the Tisza at Tápé in June, but only in subordinate amounts at Szeged it played a still less important role. In July it occurred at all three sampling sites in smaller and larger quantities amounting on the average to 2—4 mg/l. In August it increased in certain cases, particularly at the section of the Tisza at Szeged to 8—9 mg/l. In September it again diminished to the minimum failing completely at several samples from the Maros. With the exception of the periods mentioned the carbonate ion failed to occur in either of the rivers.

Concerning the sulphate ion in general the values were almost corresponding in both rivers amounting to about 30 mg/l. In the Tisza at Tápé the maximum was 41,59 mg/l on July 28th, whereas in the Maros after the flowing down of the winter tide it amounted to 60,17 mg/l on March 14th.

After the flowing down of the spring tide at Tápé somewhat higher values were obtained throughout the measurements than in the Maros, in the course of the autumn tides on the other hand those of the Maros were higher.

Phosphate ion occurred only in very slight quantities amounting to 0.1–0.2 mg/l in both rivers. This amount increased rather in the course of the autumn and winter months.

At high water level the degree of alkalinity was lower and at low water level higher in both rivers, thus both the Tisza and the Maros showed in the summer a higher degree of alkalinity, the maximum was also reached in the summer and autumn, respectively, amounting to  $3.87^\circ$  in the Tisza at Tápé on September 8th and to  $3.60^\circ$  in the Maros at Deszk on September 3rd. With the exception of a few cases the degree of alkalinity of the Tisza exceeded that of the Maros. In the Tisza at Szeged at permanently high water levels the degree of alkalinity remained constant  $1.6^\circ$ .

The degree of the hardness of water corresponded like that of the alkalinity to the water level. In both rivers the degrees of hardness were the whole year round save for slight fluctuation approximately similar. The degrees of hardness rose gradually after the flowing down of the spring tide. Reaching the maximum in both rivers in September.

Silicon could generally be found in larger quantities in the Maros, than in the Tisza. In the Maros it amounted to 11–12 mg/l, in the Tisza at Tápé to 7–9 mg/l.

The term insoluble residue involves the clayey fragments probably colloidal clayey fragments which passed into the filtrate at the filtering and could be found as residue at the determination of the silicic acid. They reached their maximum — as anticipated — when the clayey, muddy traction of the floating material increased. In such cases, owing to the presence of the colloid substances, the water sample did not clear for weeks.

The oxygen value needed for the oxidation of the whole organic substance was less in the case of high water levels. In general it occurred in amounts of about 6 mg/l.

The free oxygen was determined once a month. The obtained values were always approximately the same 6–8 mg/l in both rivers. At low water temperatures the values were usually higher.

The free carbon dioxide content was estimated once a month at the site of the sampling. For the determination samples were taken vertically from three different depths: the bottom, the middle level and the surface. Our investigations showed that regularly the samples from the bottom taken along the current contained the least carbon dioxide, and those from the surface the most. On the other hand, in the case of the vertical ones not taken along the current the opposite could not always be proved. In the second half of June the Maros did not contain any, and the Tisza at Tápé and Szeged only very slight amounts of free carbon dioxide. In July and August it failed to occur in both rivers. The maximum free carbon dioxide content in the winter months was: at Tápé 8.80 mg/l in January, in the Maros 5.90 mg/l in February and at Szeged 7.00 mg/l in March.

From the analyses taken at all three sites of sampling the average value of the cations and anions was calculated both at high and low water levels. The values obtained were plotted on circular diagrams which also illustrate plausibly the difference between the Tisza and Maros and the influence exerted by the latter on the section of the Tisza at Szeged.



At high water levels at Tápé in the Tisza the calcium ion plays the most significant, the magnesium- and sodium ion a more subordinate role. The potassium ion amounts to hardly 5 per cent of the total cations, whereas the iron ion only occurs in quite insignificant amounts. Simultaneously in the Maros, in addition to the calcium ion, the sodium ion also plays an appreciable role, the magnesium- and potassium ions being present to the same extent as in the Tisza at Tápé. The amount of the iron ion is also in this case minimal. At the section of the Tisza at Szeged owing to the influence of the Tisza, the calcium ion can be found in large amounts, and as a result of that of the Maros the amount of the sodium ions also increases. (Fig. 3.)

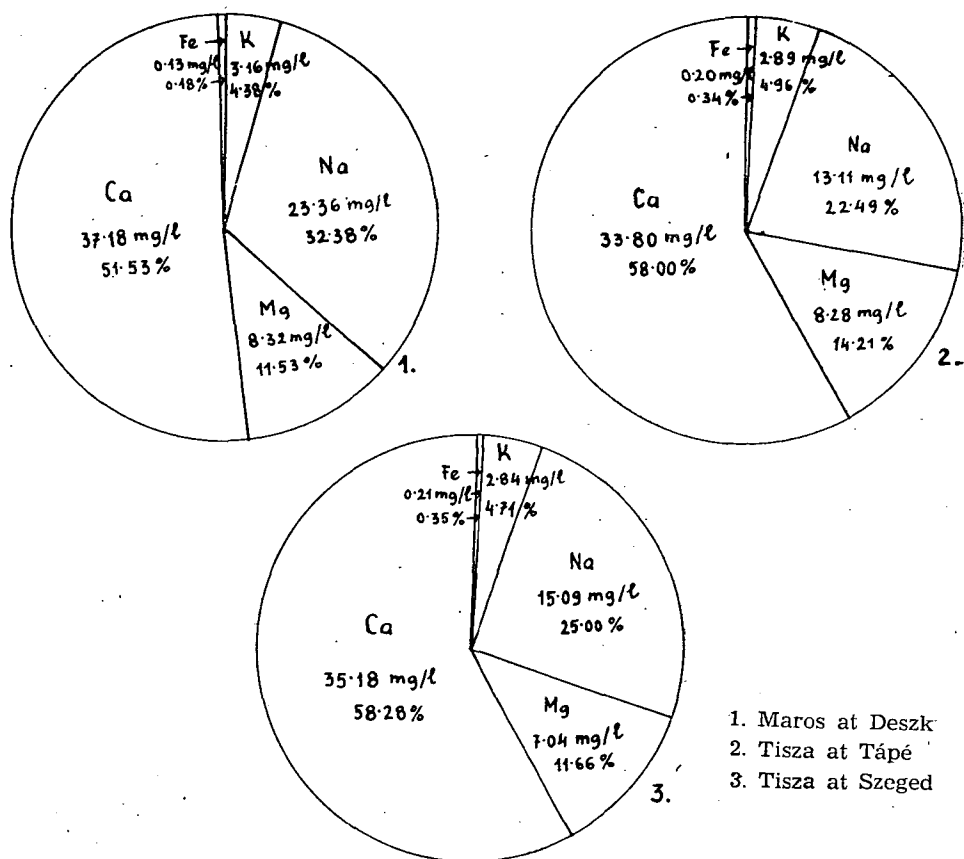


Fig. 3.

The change of the anions is interesting too. In both rivers the hydrocarbonate anion dominates. In this section the change in amount of the chlorine- and sulphate ions characterises the rivers. In the Tisza at Tápé the amount of the sulphate ions present is one and a half times as much as of the chlorine ions, in the Maros on the other hand that of the chlorine ions is two and a half times that of the sulphate ions. At the section of the Tisza at Szeged the higher chlorine ion content of the Maros becomes distinctly conspicuous. (Fig. 4.)

At low water levels the cation ratio remains about the same as it was at high water levels in both rivers. The only exception is the iron ion which failed to occur at low water levels in summer. A difference which can be detected between the high and low water levels is that as a consequence of the higher salt concentration the individual cations increase also quantitatively. (Fig. 5.)

In the case of the anions the hydrocarbonate ion also dominates, although in the Maros its amount calculated in per cents is ten per cent less. The change of the chlorine- and sulphate ions show the same regularities as recorded at high water levels. As the low water levels occur in summer the carbonate ion could naturally be found in both rivers in smaller or larger quantities. (Fig. 6.)

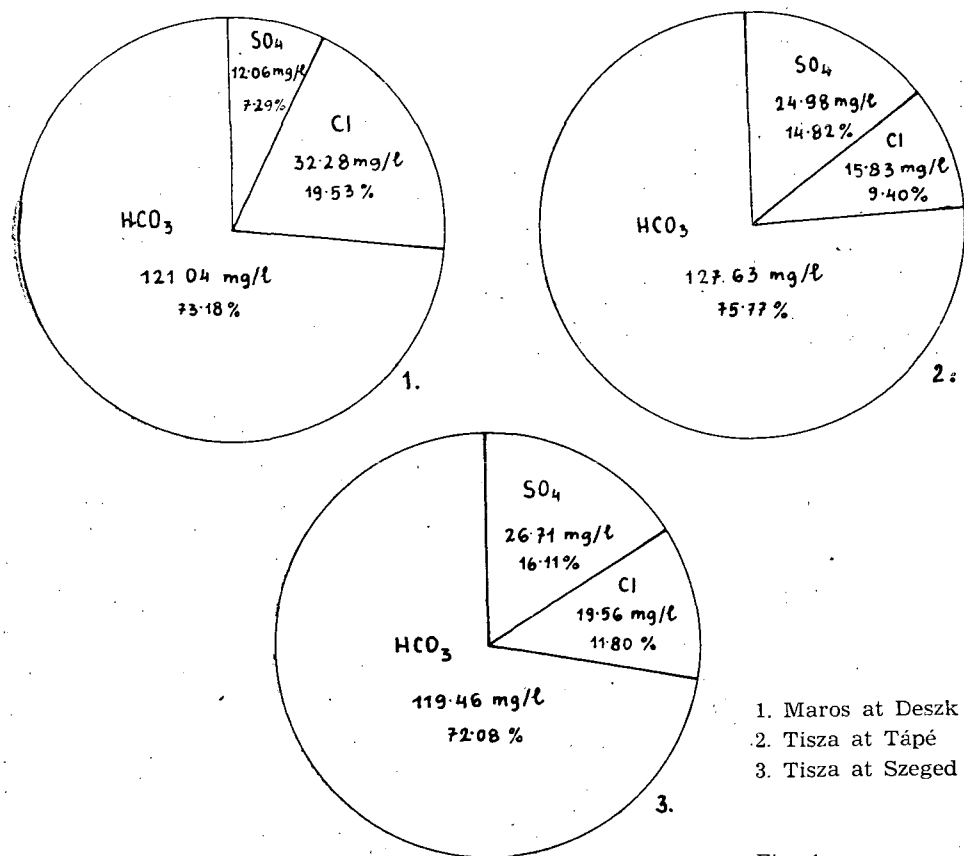


Fig. 4.

The chemical composition of the Tisza and Maros at high water levels was plotted in cation- and anion equivalent per cents on the triangular diagram suggested by Szádeczky. The Tisza can be plotted at Tápe at low water levels and at Szeged at both low and high water levels by means of straight lines running parallel, demonstrating that the ratio between the different cations and anions does not change at high and low water levels and that therefore the shift can only be quantitative. At high water levels owing

to the relatively higher chlorine content the Tisza at Tápé could be plotted with a curve running in a different direction. The Maros on the other hand, behaved differently at high than at low water levels. At high water levels the ratio of the sulphate-chlorine ion was 1:3, at low water levels it was approximately 1:2. In the case of the Maros therefore, not only the amount of the cations and anions changed, but their ratio too. (Fig. 7.)

Hence on the basis of our examinations, the following establishments could be made:

The investigations of the dissolved salts also supports our previous statements, based on the examinations of the floating material, that the Tisza and Maros possess diverging characteristics.

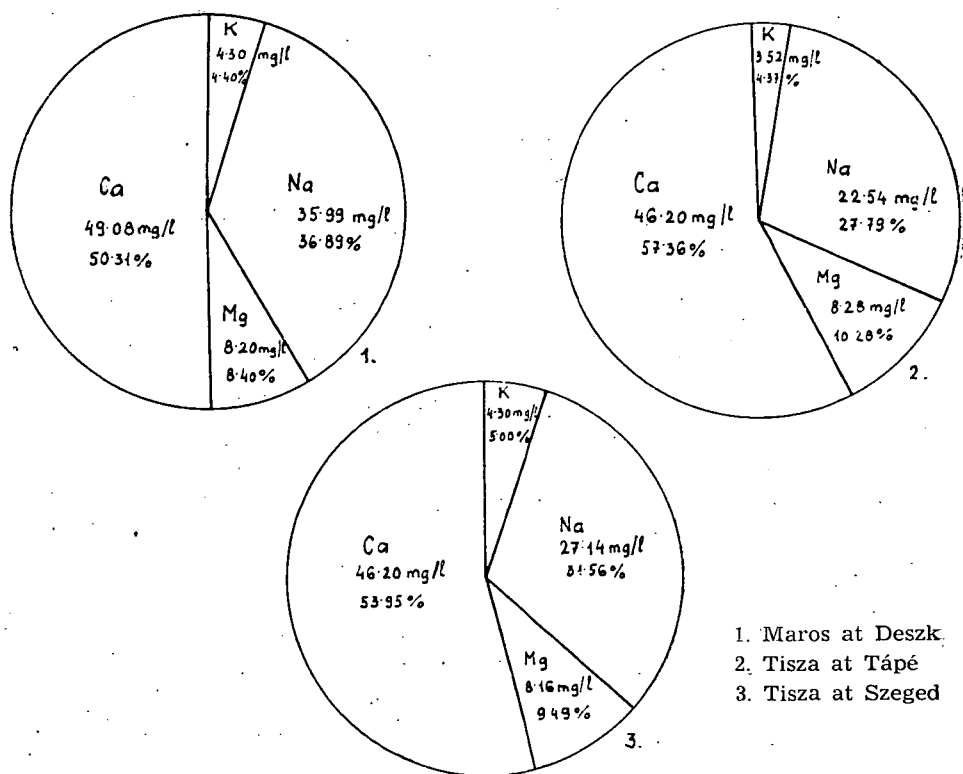


Fig. 5.

In the smaller water masses of the Maros the dissolved salt concentration is higher than in those of the Tisza at Tápé or Szeged.

The Maros always contains more sodium- and chloride ions than the Tisza proving that the dissolved salts of the Maros reach the mouth in spite of the fact that it deposits its floating material at Mezőség. The close correspondence of the equivalents of the sodium- and potassium-, as well as the chloride ions points to the fact that the sodium- and potassium ions contained in the Maros are primarily bound in the form of chloride and only to a smaller extent as sulphate. In the Tisza the sodium- and potassium ion con-



tent is lower. Here not only the chloride ions but the sulphate ones play a significant role. The sodium- and potassium ions are partly bound as chlorides and partly as sulphates.

Hydrocarbonate ions do not occur in the Tisza or in the Maros bound to sodium ions as the total sum of calcium and magnesium ions exceeded in each case that of the hydrocarbonate- and carbonate ions.

The ratio of the alkalies showed the following figures: in the Tisza the sodium- and potassium ion ratio was 4,31 at high water levels, at low ones 6,40. Lithium occurred in slight traces, rubidium and caesium failed completely. In the Maros the sodium- and potassium ion ratio was to that of the Tisza showing merely a quantitative divergence which is a characteristic property of this river. The Maros contains more potassium ions than the Tisza

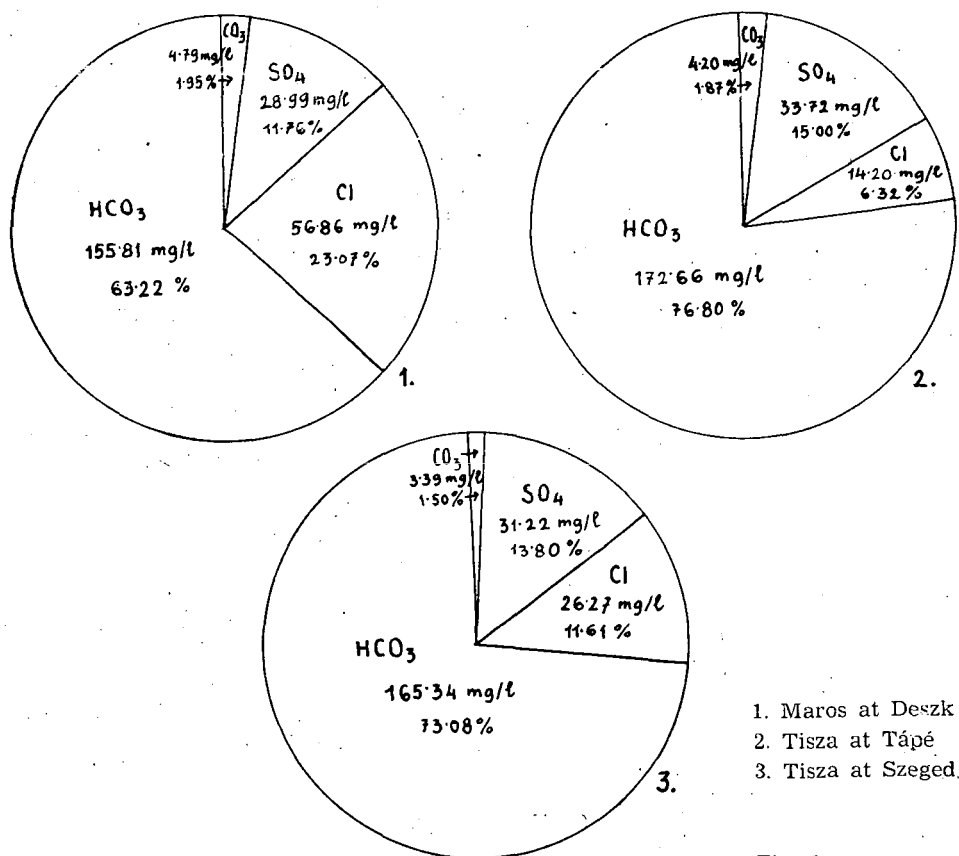


Fig. 6.

at Tápe, however, as a result of the high sodium ion content the ratio was 7,02 at high water levels and 8,80 at low ones. Hence even the smaller value is higher than the sodium- and potassium ion ratio figure relating to the summer period of the Tisza. In the Maros lithium, rubidium and caesium failed completely. At Szeged the Tisza, as anticipated, illustrated the influence exerted by the Maros. At high water levels the sodium- and potassium ion ratio figure was 5,11, at low levels 6,37. Lithium, rubidium and caesium did not

occur. Minerals containing lithium could be found in the floating material of both the Maros and Tisza, owing to the prolonged time of transport it dissolved in the latter, whereas in the former the relatively short transport period, as well as the circumstances were not favourable for the dissolution.

The divergent characteristics of the two rivers could be observed too — if also not so distinctly — and magnesium ion relation. At high water levels at Tápé in the Tisza the ratio was 3,89 and 5,59 at low ones. Of the trace elements barium could be detected in very considerable amounts, strontium to a lesser extent, whereas berillium failed to occur. In the Maros the ratio figure was 4,22 at high water levels and 5,99 at low ones. Spectroanalytical investigations also only demonstrated the occurrence of strontium and barium, berillium could not either be detected by these means. At Szeged in the Tisza

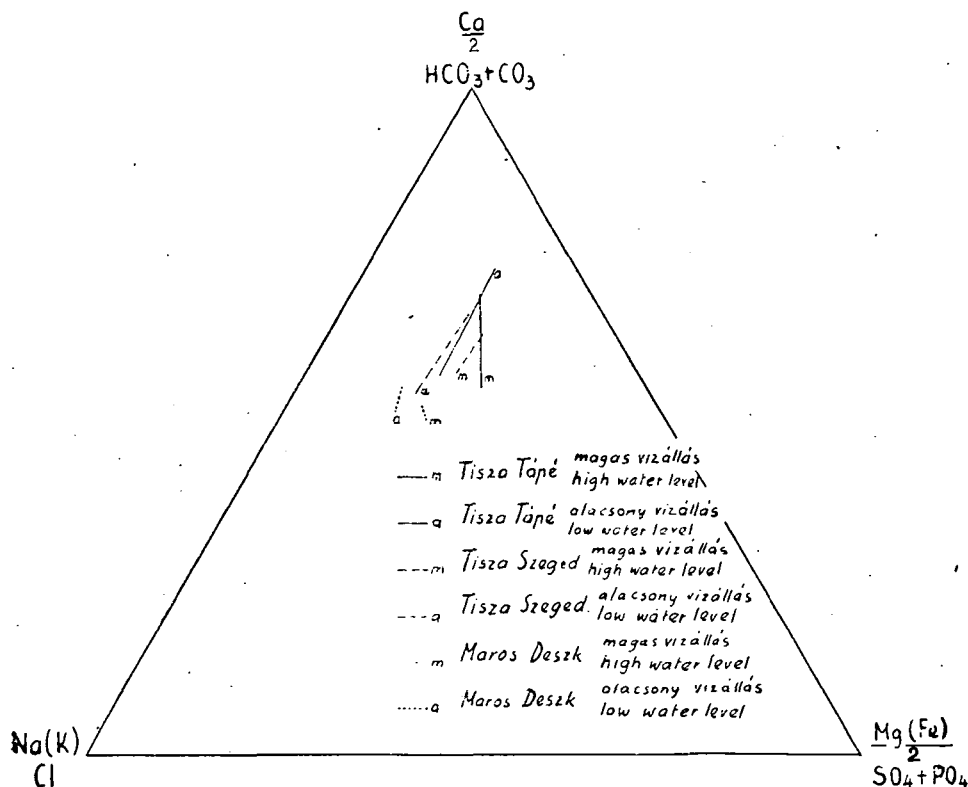


Fig. 7.

the ratio of the rare earth metals was as follows. At high water levels its ratio figure was like those quoted above lower, amounting to 4,84, at low levels it was 5,69. Of the trace elements strontium showed a distinct band barium a less distinct one, berillium failed to occur.

Salts containing the cations enumerated above, and among the anions the chloride and sulphate anions dissolve readily, in the course of the transport they always remain in solution. At the convergence of different waters, at the most, their concentration changes. However, iron and manganese behave differently.

The precipitation of iron, as has also been established by Szádeczky, starts at low pH values it is precipitated as  $\text{Fe}(\text{OH})_3$ .  $\text{Fe}(\text{OH})_2$  can separate at pH 6 in the case of a low redox potential, at higher redox potentials it is converted into ferrous-ferric hydroxide, i. e. later into ferric hydroxide showing a red colour.

At surface decomposition manganese separates more readily than iron it turns into solid manganese dioxide, only going again into solution at relatively high pH values.

As in the Maros and the Tisza the pH values ranged always approximately at 7 it is comprehensible that they only contained slight amounts of dissolved manganese, which could only be demonstrated qualitatively. Owing to the fact that iron can only dissolve in the case of low redox potentials at pH values exceeding 6, it is natural that in both the Tisza and Maros it could be found in larger or smaller quantities.

The water of both rivers is often used for irrigation. Therefore the composition of the water of the rivers was also examined from this point of view. As mentioned above in the Tisza the sodium ions are mostly bound to sulphate and to a lesser extent to chloride, whereas the calcium- and magnesium ions are bound to hydrocarbonate and carbonate respectively.

The danger of the soil becoming saturated with soda has thus not to be taken into account. At the irrigation period the ratio prevailing between the rare earth metals and the alkaline metals is at least twofold. In the Maros the alkalis are in the first place bound to chloride and secondarily to sulphate. The greater part of the calcium- and magnesium ions is also bound to hydrocarbonate- and carbonate ions, respectively. The ratio between the rare earth metals and the alkaline metals is one and a half fold during the irrigation period, hence the water of the Maros seems also suitable for irrigation. Furthermore considering that the potassium ion content of the Maros is high at this period and that this element is an important factor from the point of view of cultivation, the water of the Maros is very appropriate for irrigation, nevertheless, the relatively low water content must be regarded as an inhibiting circumstance.

The floating material of the different water samples was separated by pipetting into 8 fractions. Fig. 8. illustrates the 8 fractions grouped for the sake of perspicuity in three parts. The first part contains the granules not exceeding 0,002 mm in diameter, the clayey fraction, the second part the fractions ranging between 0,002—0,0116 mm in diameter, the muddy fraction, and finally the third part the granules exceeding 0,016 mm in diameter, the sandy fraction.

Owing to the reasons mentioned above at the periods of high water levels the taking of water samples was discontinued at Tápé in the Tisza and at Deszk in the Maros, hence continuous examination could only be carried out from the section of the Tisza at Szeged.

Earlier statements that the amount of the floating material is also a function of the water level were supported. Changes diverging from this assumption — as also indicated in our previous examinations — are due to the changes of the weather.

At Tápé during the period of the investigations the amount of the floating material of the Tisza never attained the concentration of the water samples taken at Szeged or Deszk. The maximum fell into the period of the winter tide it was 580 mg/m<sup>3</sup> on February 25th. The fluctuations in concentration,

in the course of the first summer months, were not so much due to the water levels as rather to the weather conditions. The fluctuations of the concentration during the autumn indicated the different tide waves most appropriately. At this period the concentration hardly attained  $500 \text{ g/m}^3$ . At low water levels in January and during the summer the sandy and muddy fractions were always larger.

The character of the floating material of the Maros also differs from that of the section of the Tisza above the point of convergence. At the investigations carried out in 1951 it could be established that at low water levels the sandy, at high water levels the muddy and clayey fractions dominate in the Maros. In the course of 1952, after the investigations had been in progress for two years, this fact was again proved although the water level conditions were quite different from those of the previous year. In 1951 after the flowing down of the spring high water the water levels of the Tisza and Maros remained low the whole year round, whereas in 1952 after the running down of the spring tides the low water level lasted for a relatively short period in the summer and after the autumn rains both rivers overflowed to such an extent that the levels approached the high values of the spring. The granular composition of the floating material of the Maros usually conformed the whole year round to the changes of the tide. The concentration fluctuations of the Maros ranged between far greater limits than those of the Tisza at Tápé. Save for a few exceptions the end of June and the beginning of July they were also related to the changes of the water levels. During the above periods the spring tide of the Maros was running down and in spite of this fact the amount of the floating material was  $740 \text{ g/m}^3$ . This fact should also be attributed to the changes of the weather. The maximum fell into the high water levels of the spring, the concentration amounted to  $1140 \text{ g/m}^3$  when it was measured at the end of March.

In the course of the winter when low water levels prevailed for several months the sandy fraction of the floating material dominated in the section of the Tisza at Szeged. In addition smaller amounts of muddy portions and very slight quantities of clayey ones could also be found. During the spring tides the muddy and clayey fractions increased consequently after the flowing down of the tide the sandy fraction became less important in comparison to the significantly increased amount of the muddy fractions, thus showing the true character of the river. Owing to the joining of the two rivers the amount of floating material ranged within wide limits compared with the changes in concentration of the Tisza at Tápé. The maximum set in suddenly with the spring floods on April 1st amounting to  $1580 \text{ g/m}^3$ . During the permanent low water levels the amount of floating material had a similar concentration to that found at Tápé, at this period the domination of the sandy fraction could not be observed.

Thus the finer fractions were present in both rivers at high water levels. This can be accounted for by the fact that during these periods the rivers stirred up the muddy and clayey portions occurring in larger amounts on the flooded area. At low water levels on the other hand, when the fall of the rivers is relatively greater, a comparatively small fraction of clayey and muddy portions obtained access to the already formed river bed thus their amount diminished appreciably, whereas owing to the greater fall the rivers were capable of carrying off part of the coarser silt.



The floating material of all three sampling sites was separated into 8 fractions by means of pipetting. These were averaged at high- and low water levels. The results obtained were plotted in a sum-curve on the basis of which the following could be established.

At high water levels the sum-curve demonstrating the section of the Tisza at the convergence point can be well differentiated from the one illustrating the Maros, the two curves run almost parallel showing the different characteristics of the two rivers, i. e. the coarser granule composition of the floating material of the Maros. The sum-curve of the section of the Tisza at Szeged reflects truly the influence of the Maros, consequently its sum-curve ranges between the two previous ones. (Fig. 9.)

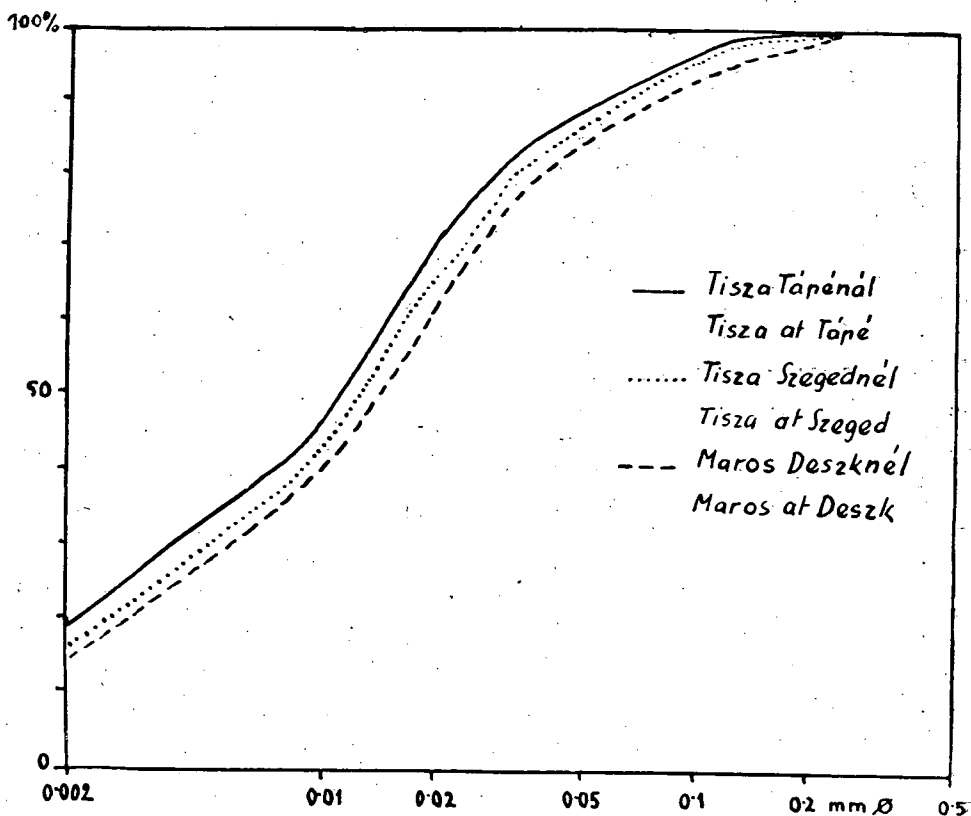


Fig. 9

At low water levels the sum-curve of the Tisza at Tápé shows that the muddy fraction is dominating, whereas in the case of the Maros the sandy fraction is more significant consequently the two curves intersect at this point. At the section of the Tisza at Szeged the sum-curve shows an almost parallel course to that illustrating the muddy and finer sandy fractions of the Maros, as a great part of the coarser sandy portion is deposited directly in the vicinity of the mouth the two curves approach closely at this section showing clearly the influence of the Maros. (Fig. 10.)

The mineral residue of the floating material of the Tisza diverges from the mineral species which can be found in the floating material of the Maros. Inasmuch as among the feldspars of the Tisza zonal plagioclases also occur abundantly, i. e. fragments originating from the tertiär volcanic region; whereas in the Maros, as already indicated in our previous investigations, the fragments originating from the andesite region of Transylvania do not reach the lower section. Garnet can only very rarely be found in the Tisza, whereas in the floating material of the Maros it occurs fairly frequently. The relatively large amount of idiomorphous zircon granules which can be found in the Tisza is striking, in the Maros this mineral plays only a subordinate role. In the Tisza, particularly at low water levels, considerable quantities of iron

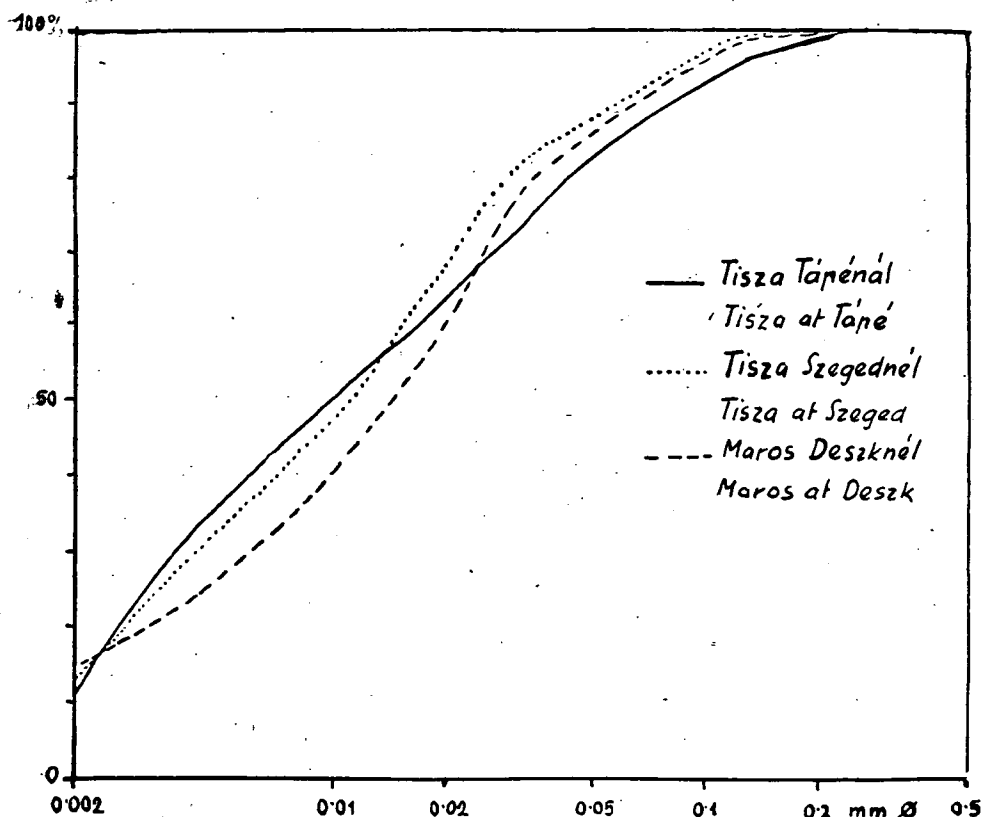


Fig. 10.

ores (magnetite, limonite) can be found. Among micas in addition to muscovite and biotite, chlorite also played a significant role.

Turmaline is a mineral rather characteristic for the Maros.

The amount of the floating material and dissolved salts of the Tisza and Maros were averaged from the samples taken in the course of the year, the following values were obtained: For sake of comparison the results measured in the Maros in 1951 are also reported.

	floating material		dissolved salts	
	1951	1952	1951	1952
Tisza at Táapé	—	0,233	0,220 g/l	0,214 g/l
Tisza at Szeged	—	0,208 g/l	0,233	0,226
Maros at Deszk	0,420	0,246	0,280	0,280

It could be established that concerning the quantity of the dissolved salts there is no essential divergence between the two years, although the weather- and water level conditions varied completely. In contrast to these findings the change in the amount of the floating material was all the more striking indicating that the amount of the floating material is in close correlation with the weather conditions and water levels.

### SUMMARY

The quantitative change of the dissolved salts is usually a function of the water level. The change in the amount of the calcium-, sodium-, potassium-, chloride-, hydrocarbonate ions is reversibly proportional. The magnesium-, sulphate- and phosphate ions are not very sensitive to changes of the water levels.

The concentration of the dissolved salt of the Maros is always higher than that of the Tisza.

In the Maros the higher sodium- and potassium content is primarily bound to the chloride ion, in the Tisza this is not only valid for the chloride ion but also for the sulphate ion. Hydrocarbonate ions are not bound in the Tisza or in the Maros bound to sodium ions, thus if the water of the rivers is used for irrigation the danger of the soil being saturated with soda must not be taken into account.

Of the trace elements lithium can be detected in slight traces in the Tisza at Táapé, whilst in the section of the Tisza at Szeged and in the Maros it failed to occur. Rubidium and caesium could not either be found in any of the three sampling sites. The Tisza at Táapé contains significant amounts of barium at the other two sampling sites it only occurred in insignificant quantities associated with strontium. Beryllium did not occur in either river.

Concerning the granular composition of the floating material the previous establishment holds good that corresponding to the characteristic of the section of the river the finer fraction dominates at high water levels and the coarser one at lower ones.

The sum-curve composed of the mean values of the individual fractions of the floating material at low and high water levels, demonstrates this characteristic convincingly.

The zonal plagioclases are characteristic components of the floating material of the Tisza, they do not occur in the Maros. The relatively large amount of zircon crystals contained in the Tisza is striking. Turmaline is a rather characteristic mineral of the Maros.

The Maros deposits a considerable part of its floating material originating in the andesite district in the Mezőség, its dissolved salts, however, proceed to the mouth

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## ИССЛЕДОВАНИЕ МАТЕРИАЛА, НЕСЕННОГО ТИССЕЙ И МАРОШЕМ В РАСТВОРЁННОМ СОСТОЯНИИ.

— ИОСИФ МЕЗЭШИ И ЭВА ДОНАТ —

Количественные изменения растворенных солей, как правило, находятся в зависимости от горизонта воды. Горизонтам воды обратно пропорциональны изменения количеств ионов кальция, натрия, калия, хлорида и гидрокарбоната и прямо пропорционально изменение количества ионов железа. Ионы сульфата, фосфата и магнезия к изменениям горизонта воды не чувствительны.

В реке Марош более высокие количества натрия и калия обусловлены хлористым ионом, а в Тиссе играет роль, кроме хлористого иона, и сульфат-ион.

Количество гидрокарбоната ни в Тиссе, ни в Мароше ионом натрия не обуславливается:

Из элементов, присутствующих в следах, появляются на участке Тиссы при Тапэ-барий, литий и стронций, а в Мароше только стронций.

Соответственно секционному характеру обеих рек, при высоком уровне воды преобладающая фракция — более мелкая, а в низком — более грубая, в взвешенных наносах.

Для минеральных компонентов материала взвешенных наносов характерны зонные плагиоклазы, отсутствующие в Мароше.



Table 2.

Szeged	dissolved salts	alkalinity	variable hardness	total hardness	Ca-ion	Mg-ion	Na-ion	K-ion	R <sub>2</sub> O <sub>3</sub>	iron	manganese	HCO <sub>3</sub> -ion	CO <sub>3</sub> -ion	Cl-ion	SO <sub>4</sub> -ion	PO <sub>4</sub> -ion	SiO <sub>2</sub>	insoluble residue	organic matter	free oxygen	free CO <sub>2</sub>
I. 30.	0,13	2,51	5,12	8,46	45,93	9,32	20,01	3,89	—	0,05	—	153,13	—	34,00	34,20	0,06	6,40	4,00	6,68	—	6,70
I. 28.	0,13	2,06	5,78	6,99	36,14	8,43	15,59	3,44	6,80	0,08	—	125,68	—	19,50	34,14	0,05	12,00	3,20	8,82	8,86	5,90
III. 5.	0,29	2,13	5,97	7,20	36,93	8,85	19,23	3,10	9,00	—	—	129,95	—	25,80	33,40	—	2,80	12,40	2,93	—	—
III. 12.	0,38	2,61	7,31	8,00	44,90	9,61	21,90	4,32	18,40	—	—	159,24	—	35,10	35,29	—	9,80	3,40	4,74	—	—
III. 19.	0,13	2,67	7,48	8,54	44,90	10,58	24,72	7,28	2,60	—	ny	162,89	—	38,40	29,53	0,18	7,40	6,00	2,50	—	—
III. 26.	0,30	2,36	6,61	7,86	44,90	8,70	23,66	3,81	6,20	0,22	—	143,98	—	38,50	30,72	0,05	7,20	5,00	2,15	7,73	7,00
IV. 2.	0,31	2,17	6,08	7,79	42,31	8,15	15,96	3,89	7,80	0,14	—	132,39	—	19,50	38,00	—	9,80	8,80	3,31	—	—
IV. 6.	0,29	1,84	5,12	6,55	35,34	7,00	10,36	2,82	6,80	0,63	—	112,26	—	11,40	23,00	—	13,80	4,40	2,36	—	—
IV. 12.	0,18	1,64	4,60	6,13	30,44	8,14	—	—	6,60	0,29	—	100,06	—	11,50	29,90	—	8,50	8,20	4,82	—	—
IV. 21.	0,24	1,63	4,57	6,12	32,07	7,14	9,79	3,10	6,10	0,26	—	99,45	—	12,50	22,29	0,12	7,00	13,10	2,30	—	—
IV. 28.	0,28	1,63	4,57	5,95	31,58	6,66	13,26	2,00	6,20	0,11	—	100,06	—	18,30	16,60	0,02	9,50	2,30	2,03	6,95	3,00
V. 5.	0,20	1,64	4,60	5,54	30,17	5,76	11,02	1,97	4,60	0,92	—	100,06	—	21,60	20,22	—	8,40	2,00	3,96	—	—
V. 14.	0,36	1,82	5,09	6,16	34,36	5,89	16,31	3,44	5,40	0,14	—	111,04	—	17,40	31,02	—	17,00	4,10	3,44	—	—
V. 21.	0,25	1,84	5,15	6,49	37,63	6,34	8,33	1,81	5,60	0,13	—	112,26	—	11,80	27,88	—	7,40	3,50	3,92	—	—
V. 28.	0,22	2,05	5,74	6,97	39,09	8,01	11,29	1,83	5,00	0,14	—	125,07	—	19,40	26,57	—	9,60	4,40	3,07	6,22	4,40
VI. 4.	0,18	2,34	6,56	7,77	41,44	8,58	15,04	3,65	3,80	0,16	—	142,76	—	24,40	31,70	—	8,60	1,16	7,75	—	—
VI. 11.	0,16	1,99	5,58	7,08	35,75	9,06	21,28	2,68	3,00	0,04	—	121,39	—	30,50	26,80	—	6,00	3,60	8,51	—	—
VI. 18.	0,19	2,23	6,24	7,89	39,99	10,03	21,16	3,05	3,10	0,07	—	136,03	—	29,75	33,00	—	7,30	2,00	6,44	6,50	6,02
VI. 25.	0,25	1,97	5,52	5,70	37,40	4,68	16,99	1,89	4,40	0,15	ny	120,17	4,08	20,95	24,66	—	11,00	—	4,34	—	—
VII. 2.	0,14	2,08	5,82	5,21	32,90	8,75	20,73	4,04	3,20	0,11	—	126,88	—	29,50	22,03	—	8,60	2,30	4,21	—	—
VII. 9.	0,23	2,23	6,24	8,06	39,04	11,32	18,80	3,79	3,50	0,16	—	138,47	3,06	25,30	30,62	—	8,70	5,90	2,42	—	—
VII. 16.	0,21	2,60	7,27	8,69	45,50	10,12	24,93	6,72	—	0,22	—	160,43	1,08	39,40	33,20	—	6,20	2,30	6,66	7,11	—
VII. 23.	0,22	2,32	6,49	9,26	46,60	11,92	25,81	4,61	6,50	0,37	ny	148,02	14,07	47,20	30,60	—	4,00	7,00	7,08	—	—
VII. 30.	0,31	3,01	8,42	10,89	56,10	13,24	21,96	3,87	6,00	0,04	—	183,43	7,99	27,60	36,66	—	11,90	3,00	6,20	—	—
VIII. 6.	0,26	2,86	8,01	8,93	50,60	8,09	28,79	3,84	1,80	0,08	—	174,46	3,03	25,98	34,52	—	7,60	2,20	4,50	—	—
VIII. 13.	0,27	2,91	8,15	9,06	52,60	8,60	30,26	3,56	0,80	0,10	—	177,51	9,30	27,77	34,20	—	7,90	1,70	4,20	—	—
VIII. 19.	0,26	3,27	9,16	7,57	41,55	7,67	33,91	6,16	3,00	0,06	—	161,95	4,94	27,13	34,20	—	7,00	3,80	4,40	—	—
VIII. 27.	0,32	3,32	9,29	8,74	51,90	6,47	28,58	3,22	0,90	0,06	—	185,31	2,21	23,99	34,20	—	9,00	—	5,50	10,40	—
IX. 3.	0,33	3,60	10,08	9,71	56,99	7,59	32,69	4,38	4,70	0,09	—	201,91	—	24,60	34,40	0,01	7,50	5,30	6,42	—	—
IX. 10.	0,45	3,44	9,63	9,49	58,70	5,54	35,58	5,23	5,50	0,06	—	197,50	1,91	24,20	34,50	0,02	7,70	1,20	4,38	—	—
IX. 17.	0,30	3,33	9,32	8,51	50,90	6,07	33,52	3,93	4,30	0,06	—	186,05	0,85	22,30	33,80	0,06	6,60	2,00	5,17	—	—
IX. 24.	0,30	3,03	8,57	9,52	49,60	12,10	26,70	4,86	5,40	0,07	—	186,66	1,09	23,30	32,80	0,03	3,70	3,30	6,88	—	—
X. 1.	0,27	2,69	7,53	7,90	45,72	4,22	27,64	4,38	1,40	0,10	(ny)	164,09	—	21,40	26,80	0,07	6,30	3,00	4,08	6,76	4,45
X. 8.	0,29	1,94	5,43	6,17	33,27	6,63	12,92	2,66	4,90	0,35	—	118,34	—	10,40	23,20	0,02	6,80	6,80	4,60	—	—
X. 15.	0,25	2,11	5,91	5,91	33,42	5,36	25,43	3,02	4,30	0,05	—	128,71	—	19,30	21,20	—	4,40	4,40	2,93	—	—
X. 22.	0,30	2,18	6,10	6,84	37,27	7,11	18,02	3,28	6,80	0,08	—	132,98	—	22,00	26,20	0,02	10,10	5,00	4,05	—	—
X. 29.	0,14	1,65	4,62	5,37	29,30	5,53	10,07	2,83	3,60	0,18	—	102,48	—	14,40	20,49	0,06	8,50	4,20	4,78	2,12	—
XI. 4.	0,14	1,64	4,60	5,07	27,67	5,23	11,49	1,10	1,40	0,29	—	100,04	—	13,60	17,30	0,01	9,00	6,80	4,46	—	—
XI. 12.	0,11	1,83	5,12	5,54	30,20	5,77	12,94	3,52	2,90	0,19	—	111,63	—	15,25	20,70	0,01	6,50	0,60	2,94	—	—
XI. 19.	0,12	1,44	4,03	4,76	24,58	5,10	12,67	1,63	3,04	0,26	—	87,84	—	14,90	17,00	0,01	12,20	3,10	3,27	—	—
XI. 28.	0,17	1,74	4,87	5,66	33,66	4,13	9,40	1,99	8,71	0,14	—	106,14	—	10,90	22,52	0,02	10,10	5,60	3,92	—	—
XII. 3.	0,22	1,79	5,01	5,54	33,51	3,71	10,78	1,66	8,56	0,08	—	109,18	—	12,20	21,04	0,02	11,30	0,90	3,55	—	—
XII. 9.	0,15	1,66	4,65	4,94	30,24	3,28	9,95	2,62	7,57	0,33	—	101,26	—	10,89	18,60	0,02	5,80	1,30	3,67	—	—
XII. 18.	0,15	2,07	5,80	6,69	37,04	7,23	14,50	2,54	11,43	0,03	—	126,27	—	15,70	30,08	0,01	8,30	0,20	3,50	—	—
XII. 22.	0,20	1,69	4,73	5,07	28,81	6,26	9,61	1,55	5,77	0,35	—	103,99	—	8,10	23,18	0,01	5,60	12,40	3,86	—	—
XII. 30.	0,14	1,66	4,65	5,91	26,96	7,78	8,58	2,52	6,61	0,33	—	101,26	—	7,30	25,15	0,01	5,40	5,90	3,59	—	—

Table 1.

Tapé	dissolved salts	alkalinity	variable hardness	total hardness	Ca-ion	Mg-ion	Na-ion	K-ion	R <sub>2</sub> O <sub>3</sub>	iron	manga- nese	HCO <sub>3</sub> - ion	CO <sub>3</sub> -ion	Cl-ion	SO <sub>4</sub> -ion	PO <sub>4</sub> -ion	SiO <sub>2</sub>	insoluble residue	organic matter	free oxygen	free CO <sub>2</sub>
I. 28.	0,11	2,63	7,36	7,57	41,15	7,88	19,93	3,91	11,20	0,08	ny	160,14	—	14,90	34,30	0,11	7,20	3,60	10,41	7,63	8,80
II. 25.	0,11	2,01	5,63	5,72	27,00	7,49	12,04	3,33	10,00	0,32	ny	122,85	—	9,50	26,47	0,12	12,40	3,20	6,24	7,41	21,50
III. 3.	0,11	2,30	6,43	6,96	31,81	10,94	15,54	4,18	7,20	—	—	139,99	—	14,40	30,68	0,14	11,80	5,00	2,37	—	—
III. 10.	0,13	2,32	6,48	7,51	37,68	9,67	19,55	3,98	6,00	—	—	141,24	—	27,20	35,50	—	10,40	5,40	2,72	—	—
III. 17.	0,11	2,88	8,05	9,53	47,56	12,54	18,01	5,42	3,10	—	(ny)	175,44	—	26,50	41,10	—	5,80	7,60	10,21	—	—
III. 24.	0,26	2,46	6,88	9,37	40,14	16,37	9,64	2,51	2,40	0,08	—	149,96	—	23,20	35,51	—	6,80	6,40	2,50	6,84	4,80
III. 31.	0,20	2,18	6,12	6,43	29,48	10,09	13,08	4,88	13,20	—	—	133,22	—	14,40	19,73	0,14	11,20	20,00	3,05	—	—
V. 12.	0,19	2,18	6,10	5,99	34,85	6,06	13,22	2,09	5,10	0,07	—	132,92	—	11,00	23,18	—	5,20	3,40	3,16	—	—
V. 19.	0,15	2,19	6,13	6,73	39,08	6,94	12,76	2,71	5,80	0,31	—	116,57	—	17,10	27,45	—	10,40	5,00	3,98	—	—
V. 26.	0,19	2,22	6,20	6,93	37,57	7,34	14,83	3,98	5,20	0,34	—	135,12	—	17,40	28,10	0,12	9,00	2,40	4,01	5,72	7,70
VI. 2.	0,21	2,41	6,76	8,36	42,79	10,33	15,19	2,88	5,60	0,22	—	147,19	—	19,30	31,89	—	4,80	6,40	5,12	—	—
VI. 9.	0,16	2,45	6,85	7,70	36,08	11,37	20,73	3,98	2,60	0,06	—	149,45	—	23,20	30,74	—	4,20	3,90	4,23	—	—
VI. 16.	0,27	1,66	4,65	5,44	30,70	6,69	24,23	4,09	2,60	0,03	—	101,26	—	46,85	23,67	—	7,60	4,30	5,82	6,77	3,58
VI. 23.	0,12	2,13	5,96	6,65	33,95	8,27	14,51	3,36	3,20	0,21	—	123,83	1,80	22,90	24,66	—	6,20	1,40	4,02	—	—
VI. 30.	0,16	2,10	5,89	7,60	39,40	9,12	11,61	3,19	2,80	0,07	(ny)	113,46	4,80	17,35	21,37	—	7,60	2,40	2,86	—	—
VII. 7.	0,18	2,24	6,27	6,90	29,80	11,49	17,10	3,53	2,70	0,06	—	136,64	3,60	18,40	26,96	—	6,60	6,00	2,42	—	—
VII. 14.	0,37	1,74	4,87	6,27	27,74	10,03	30,23	4,01	3,40	0,04	—	102,48	1,80	50,60	26,14	—	11,80	3,40	5,14	7,86	—
VII. 21.	0,24	2,95	8,26	9,47	47,29	12,44	23,05	6,92	3,80	0,16	(ny)	179,05	7,80	26,00	31,56	—	6,50	3,70	6,47	—	—
VII. 28.	0,29	3,26	9,13	10,74	56,10	13,24	21,96	3,87	2,00	0,08	—	198,86	11,18	10,83	41,59	—	9,70	2,90	3,90	—	—
VIII. 4.	0,36	3,37	9,44	7,44	52,60	0,36	30,32	3,08	1,60	0,09	—	205,57	4,94	15,82	35,51	—	9,90	2,10	3,50	—	—
VIII. 11.	0,44	3,38	9,46	9,00	51,95	7,54	26,51	3,36	2,80	0,06	—	193,37	6,30	10,62	38,31	—	5,50	3,80	4,30	—	—
VIII. 18.	0,30	3,37	9,44	8,72	49,70	7,72	24,52	4,69	2,80	0,05	—	178,41	5,48	14,01	36,99	—	6,90	1,10	4,90	—	—
VIII. 25.	0,26	3,51	9,83	9,74	52,30	10,07	23,78	3,65	1,90	0,08	—	202,52	5,21	9,44	40,11	—	6,70	1,10	4,20	9,38	—
IX. 1.	0,28	3,32	9,30	9,52	55,60	7,59	24,12	4,01	6,50	0,02	—	202,52	0,55	9,60	36,80	0,01	8,70	2,40	5,95	—	—
IX. 8.	0,38	3,87	10,84	9,28	55,50	6,63	32,35	3,76	6,00	0,02	—	201,30	0,55	12,58	36,20	0,01	6,00	1,60	4,47	—	—
IX. 15.	0,31	3,64	10,19	8,72	51,45	6,63	26,59	4,46	5,10	0,02	—	185,47	1,12	10,80	35,20	0,04	6,40	1,20	4,99	—	—
IX. 22.	0,33	2,84	7,95	7,49	38,34	9,30	23,90	1,07	—	0,08	—	163,24	2,21	9,20	36,40	0,05	4,60	2,20	5,19	—	—
IX. 29.	0,39	2,89	8,09	8,15	51,50	4,16	22,02	3,84	—	0,16	—	176,29	—	11,30	36,40	0,01	7,00	3,20	5,38	10,31	5,08
X. 6.	0,34	2,47	6,91	7,02	44,84	4,16	8,97	2,71	2,00	0,22	—	150,67	—	2,10	19,60	0,01	12,00	5,20	2,91	—	—
X. 13.	0,29	1,90	5,32	5,88	31,07	4,22	10,41	3,06	8,80	0,31	—	115,90	—	2,60	24,00	0,01	6,00	7,20	2,39	—	—
X. 20.	0,22	2,28	6,38	7,01	37,39	7,78	11,68	3,08	1,80	0,12	—	139,08	—	14,10	22,40	0,02	7,80	4,60	4,54	—	—
X. 27.	0,16	1,91	5,35	6,15	32,29	7,11	8,93	3,19	4,80	0,17	—	116,57	—	10,34	22,61	0,01	6,90	7,90	4,68	10,02	—
XI. 3.	0,10	1,82	5,09	4,83	26,50	4,92	7,18	1,44	5,00	0,32	—	111,02	—	6,30	17,70	0,01	12,00	4,50	4,26	—	—
XI. 11.	0,15	1,81	5,07	5,36	28,14	6,26	6,25	2,60	5,20	0,26	—	110,41	—	8,40	10,70	0,01	10,00	2,80	3,80	—	—
XI. 17.	0,15	1,84	5,15	5,70	29,12	7,11	10,74	1,16	2,40	0,21	—	112,24	—	10,80	19,30	0,01	8,70	2,60	3,44	—	—
XI. 26.	0,13	1,81	5,07	5,15	26,70	7,24	9,21	1,75	7,78	0,28	—	110,96	—	6,30	16,60	0,02	7,30	9,80	4,19	—	—
XII. 1.	0,13	1,74	4,87	5,24	—	—	7,24	2,34	10,25	0,18	—	106,14	—	5,80	21,54	0,01	9,60	4,00	3,75	—	—
XII. 8.	0,14	1,72	4,82	5,07	27,12	6,62	8,24	2,29	6,59	0,32	—	104,92	—	6,70	18,91	0,01	2,80	13,10	3,07	—	—
XII. 16.	0,17	1,86	5,21	5,61	32,18	4,87	10,95	1,19	8,74	0,07	—	113,46	—	8,70	23,34	0,01	10,40	2,00	4,38	—	—
XII. 22.	0,18	1,89	5,29	5,91	32,82	5,78	9,40	2,15	12,47	0,57	—	115,30	—	7,70	20,55	0,01	7,00	11,00	3,18	—	—
XII. 30.	0,24	1,76	4,93	5,66	28,07	8,21	7,71	2,67	8,29	0,46	—	107,36	—	7,02	21,37	0,01	4,20	13,40	3,51	—	—

Table 3.

Maros	dissolved salts	alkalinity	variable hardness	total hardness	Ga-ion	Mg-ion	Na-ion	K-ion	R <sub>2</sub> O <sub>3</sub>	iron	manga-nese	HCO <sub>3</sub> -ion	CO <sub>3</sub> -ion	Cl-ion	SO <sub>4</sub> -ion	PO <sub>4</sub> -ion	SiO <sub>2</sub>	insoluble residue	organic matter	free oxygen	free CO <sub>2</sub>
II. 2.	0,17	2,20	6,17	7,39	39,98	7,83	38,80	2,77	5,40	0,14	—	134,47	—	70,70	11,51	0,03	12,00	5,80	6,26	7,01	3,80
II. 29.	0,16	2,27	6,37	8,71	40,81	13,06	27,82	3,91	17,20	0,26	—	138,78	—	49,50	35,84	0,24	12,80	5,60	8,18	7,56	5,90
III. 7.	0,33	2,31	6,47	10,06	55,99	9,73	36,80	4,54	9,60	—	—	141,15	—	66,60	43,03	0,07	6,80	4,80	2,34	—	—
III. 14.	0,36	2,60	7,29	11,00	58,43	12,28	40,84	1,88	—	—	—	158,78	—	66,50	60,17	—	8,00	6,80	7,75	—	—
III. 21.	0,17	2,36	6,62	9,97	49,02	11,73	39,58	4,40	4,60	—	ny	156,40	—	68,10	45,70	—	8,00	5,60	2,10	—	—
III. 28.	0,28	2,12	5,95	5,60	27,65	7,53	—	—	8,00	0,04	—	129,56	—	42,80	35,20	—	10,60	6,40	—	6,94	—
IV. 24.	0,14	1,64	4,60	6,02	32,95	6,14	10,32	3,02	6,40	0,26	—	100,22	—	13,35	24,49	—	20,99	3,80	6,07	—	—
V. 16.	0,28	1,64	4,60	6,19	27,72	10,06	16,09	3,73	5,40	0,11	—	100,22	—	28,10	23,37	—	23,30	2,20	3,79	—	—
V. 23.	0,25	1,70	4,76	7,19	35,50	9,70	14,68	3,67	7,30	0,37	—	103,76	—	31,30	32,22	—	19,60	4,30	4,26	—	—
V. 30.	0,24	1,76	4,93	7,01	37,52	7,67	14,81	4,06	4,80	0,07	—	107,30	—	32,60	28,44	0,32	19,98	2,00	2,88	6,08	3,80
VI. 6.	0,39	1,62	4,54	6,65	32,94	8,79	14,86	3,22	5,40	0,09	—	98,82	—	36,60	26,63	—	9,80	2,10	5,41	—	—
VI. 13.	0,25	2,28	6,38	6,83	31,30	10,70	18,88	3,67	3,30	0,10	—	120,78	5,07	22,40	29,59	—	5,30	2,80	6,75	—	—
VI. 20.	0,25	1,97	5,52	6,82	36,40	7,54	30,61	4,72	3,90	0,06	—	120,17	3,30	46,35	25,04	—	10,30	3,90	5,33	—	—
VI. 27.	0,23	1,75	4,90	6,77	36,25	7,42	21,90	2,85	2,90	0,07	(ny)	106,75	—	48,25	16,44	—	8,30	2,10	4,26	—	—
VII. 4.	0,27	2,14	5,99	7,96	40,99	9,73	35,61	3,61	2,40	0,03	—	130,54	—	51,30	29,43	—	13,50	2,00	3,46	—	—
VII. 11.	0,26	2,69	7,53	8,51	31,02	19,06	16,48	4,52	2,50	0,07	—	158,60	3,60	23,40	29,26	—	7,20	2,30	8,32	—	—
VII. 18.	0,31	2,35	6,58	9,13	47,64	10,76	35,42	5,34	2,40	0,07	—	123,83	1,20	79,50	28,77	—	10,00	2,20	7,62	7,15	—
VII. 25.	0,31	2,15	6,03	9,22	49,25	10,15	37,94	4,07	2,70	0,38	(ny)	99,55	1,80	78,10	30,41	—	7,80	5,20	15,23	—	—
VIII. 1.	0,38	1,91	5,35	8,85	47,90	9,36	28,27	4,67	1,70	0,09	—	160,06	1,39	52,80	25,48	—	9,90	2,80	4,70	—	—
VIII. 8.	0,37	2,33	6,52	9,06	47,85	8,21	32,59	4,24	2,30	0,08	—	142,61	—	55,67	28,77	—	15,60	2,00	4,40	—	—
VIII. 15.	0,38	2,51	7,03	8,18	48,30	6,19	38,51	3,81	2,10	0,00	—	153,11	—	58,90	26,80	—	12,10	3,70	5,50	—	—
VIII. 22.	0,39	2,49	6,97	8,13	49,01	5,53	36,84	4,01	0,70	0,03	—	151,89	—	52,80	24,50	0,01	11,60	6,40	3,50	—	—
VIII. 29.	0,36	2,65	7,42	9,41	58,30	5,47	41,53	4,92	1,30	0,03	—	161,65	7,94	58,80	32,88	—	16,90	5,90	3,90	8,25	—
IX. 5.	0,30	2,97	8,32	9,66	61,50	4,64	37,73	6,52	—	0,08	—	181,17	—	54,10	24,00	—	8,90	2,20	9,43	—	—
IX. 12.	0,43	2,76	7,73	9,33	59,90	4,16	—	—	6,20	0,09	—	168,36	—	49,70	26,80	0,07	7,30	1,70	3,97	—	—
IX. 19.	0,28	2,48	6,94	9,38	50,65	8,72	32,58	2,26	4,00	0,06	—	151,28	1,91	49,00	25,40	0,07	6,10	2,00	4,47	—	—
IX. 26.	0,31	2,85	7,98	9,66	56,62	7,59	37,45	4,82	3,42	0,07	—	173,85	—	54,70	24,40	0,02	8,70	2,00	5,21	—	—
X. 3.	0,44	2,70	7,56	8,72	52,38	6,06	47,79	4,47	2,00	0,38	(ny)	164,70	—	64,30	25,60	0,01	5,00	2,90	3,52	9,48	2,60
X. 10.	0,40	2,20	6,16	7,70	45,60	5,75	37,85	6,65	5,80	0,09	—	134,20	2,76	54,90	24,40	0,01	5,00	6,20	3,16	—	—
X. 17.	0,37	2,10	5,10	8,46	49,10	5,85	49,40	3,45	1,70	0,21	—	128,10	—	64,70	54,80	0,01	5,20	5,00	4,40	—	—
X. 24.	0,23	1,93	5,40	6,57	37,09	6,02	26,47	2,91	4,40	0,19	—	117,73	—	40,35	28,00	0,07	16,80	4,80	5,71	—	—
X. 31.	0,38	1,96	5,49	6,56	37,31	5,84	23,51	3,90	7,80	0,08	—	120,17	—	40,10	19,00	0,02	2,70	2,50	4,83	10,08	—
XI. 5.	0,24	1,84	5,15	6,18	32,53	5,41	26,44	2,66	4,10	0,08	—	112,24	—	37,10	20,50	0,02	14,30	1,20	4,64	—	—
XI. 14.	0,20	1,99	5,57	6,76	38,19	6,20	28,28	1,58	6,30	0,10	—	121,32	—	43,31	21,60	0,02	12,20	0,80	3,92	—	—
XI. 21.	0,23	1,98	5,54	7,22	42,48	6,75	27,30	2,62	7,01	0,06	—	120,78	—	50,17	25,80	0,02	11,40	0,80	2,86	—	—
XI. 29.	0,18	1,86	5,21	6,78	35,19	8,21	25,26	2,54	6,56	0,08	—	113,46	—	46,48	21,04	0,02	9,20	2,20	3,47	—	—
XII. 5.	0,15	1,82	5,10	5,82	35,77	4,08	13,36	2,12	11,58	0,35	—	111,02	—	20,69	17,76	0,01	—	—	4,20	—	—
XII. 10.	0,16	1,76	4,93	6,35	32,45	7,89	14,52	2,45	5,96	0,13	—	107,36	—	24,85	19,89	0,02	15,10	0,20	4,03	—	—
XII. 19.	0,28	1,75	4,90	6,94	33,77	9,66	16,52	2,72	7,54	0,06	—	112,85	—	28,85	26,96	0,01	11,80	1,20	3,81	—	—
XII. 23.	0,19	1,71	4,79	5,91	34,13	7,12	9,60	1,57	7,32	0,10	—	104,31	—	25,20	24,99	0,01	11,00	5,00	4,42	—	—
XII. 31.	0,20	1,76	4,93	5,82	34,88	4,38	10,62	2,46	6,00	0,03	—	107,36	—	15,80	23,84	0,01	7,80	7,60	3,61	—	—

## ELECTROGRAPHICAL ANALYSIS OF ORE TEXTURES

By Gy. GRASSELLY

### A) Chemical qualitative examination:

#### The detection of cobalt

In the course of the examinations carried out last year  $\alpha$ -nitroso- $\beta$ -naphthol proved to be the most suitable reagent for the electrographical detection of cobalt minerals. It showed a reddish-brown colourization with cobalt. Copper and ferric iron interfere with the demonstration.

In order to avoid the interference of these two ions either another reagent should be employed, or the copper and iron masked. For qualitative and quantitative analysis of cobalt potassium nitrite is a commonly used reagent. However, in the course of the electrographical examinations purposing the detection of cobalt this reagent furnished far less good results than those obtained with  $\alpha$ -nitroso- $\beta$ -naphthol. Although the gelatine paper treated with potassium nitrite showed the yellow colour characteristic for cobalt, yet on the sites of the polished sections containing iron a similar colour could also be detected, whilst on those corresponding to the granules containing copper a greenish colourization appeared. Moreover the colourization obtained with potassium nitrite was weaker and more blurred than that produced by the other reagent.

Hence the circumstances interfering with the detection of cobalt with  $\alpha$ -nitroso- $\beta$ -naphthol should be eliminated. When distinctly cobalt minerals are involved and cobalt dominates and the interfering iron and copper are at the most present in small amounts, the demonstration of cobalt is unequivocal.

However, in non-cobalt minerals — which may, however, contain cobalt impurities — it is also often essential to detect the presence or absence of cobalt. Thus for instance in the mineral association of Nagyörzsöny cobalt can be found in association with arsenopyrite. However, if it is also possible to establish the presence of cobalt by means of routine chemical qualitative analysis, the essential question with which arsenopyrite generation the cobalt is associated, with the older or with the younger remains unelucidated. This question cannot be decided by chemical or microscopical examinations. In such cases the electrographical procedure is most useful, as the reprint reflects the distribution of the ore granules truly thus rendering possible the unambiguous settling of the question. On the basis of these examinations cobalt belongs to the younger arsenopyrite generations. In order to demonstrate the cobalt contained in the arsenopyrites the iron had in the first place

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to be masked to eliminate its interference. The more so since in the case of other minerals containing iron, ferric iron interfered only to a small extent with the demonstration, whereas in the case of arsenopyrite and löllingite the reprint obtained on the paper impregnated with  $\alpha$ -nitroso- $\beta$ -naphthol showed such a dark brown colour that this might truly mask the colourization produced by the slight amount of cobalt.

The elimination of the interference of the iron is accomplished as follows: iron and cobalt form with sodium phosphate iron phosphate and cobalt phosphate respectively. Of these phosphates only cobalt phosphate reacts with the reagent, iron phosphate does not give a reaction, the faint yellow colour of the latter can hardly be detected on the gelatine paper which the action of the reagent has already turned yellow. The gelatine paper is first treated with a solution of sodium phosphate then electrolysed and subsequently immersed for a short time in the reagent solution. The examination can also be performed by immediately impregnating with the reagent, the gelatine paper treated with sodium phosphate, hereupon the excess moisture is eliminated and the electrolysis carried out. The result is satisfactory the cobalt can be readily detected without that the iron causes any interference.

Copper is the second interfering ion. It produces a brown colourization resembling that of cobalt, thus if the arsenopyrite contains scattered chalcopyrite granules these can easily be confounded with the colourization due to the cobalt impurities. The elimination of the interference is accomplished as follows: the paper is treated with a solution of potassium iodide, and then electrolysed. Cuprous iodide forms and, owing to the evolved iodide, the colour of the paper turns brown. In order to eliminate it the gelatine paper is immersed in a sodium thiosulphate, or a weakly acidified sodium sulphite solution, the excess moisture removed and the test paper introduced into a solution of the reagent.

The interfering effects exerted by iron and copper can also be eliminated simultaneously by immediately treating the gelatine paper with a solution of potassium iodide and sodium phosphate the further procedure is similar to that applied for the elimination of the interference of copper. If the polished section contained any cobalt — also only a slight amount — its characteristic colourization will appear without interference.

### The detection of iron-arsenic minerals

$\alpha$ -nitroso- $\beta$ -naphthol is not only suitable for the detection of cobalt but for that of iron-arsenic minerals (arsenopyrite, löllingite etc.) in general. Inasmuch as if an ore texture also contains these minerals granules the gelatine paper treated with the reagent shows a dark brown colourization on the sites corresponding to the granules. Hence, löllingite as well as arsenopyrite can readily be differentiated from the cobalt- and nickel arsenides with which they are easily confounded under the ore microscope. This way of detection is the more advantageous since, on the one hand it takes far less time than the individual demonstration of iron and arsenic, and on the other hand, the brown colourization appearing on the test paper treated with  $\alpha$ -nitroso- $\beta$ -naphthol could so far be detected only on the action of iron-arsenic minerals and not in the case of other minerals (smaltite, chloantite, safflorite, ullmanite, linneite, nickelite), hence the reaction is characteristic for iron-arsenic minerals.



### The detection of arsenic

Gelatine paper treated with silver nitrate is suitable for the demonstration of arsenic. Between the reagent paper and the cathode some layers of filter paper — impregnated with a solution of electrolyte — should be placed, as otherwise the silver which is extremely quickly reduced spoils the reprint. The detection of arsenic was attempted on section of löllingite, arsenopyrite, tetrahedrite, enargite and native arsenics. In contrast to the others, this reprint cannot be preserved.

### The detection of lead and bismuth

In the case of the detection of lead the fact of the surface of the ore used as anode becoming oxidized in the course of the electrolysis a lead oxide layer forming upon it caused difficulties. The potassium chromatous procedure suggested earlier did not either furnish adequate results. The benzidinous reaction which is usually a suitable procedure was also not applicable for electrographical examinations. The colourization produced on paper merely treated with potassium iodide was not either satisfactory. However, the reaction with cinchonine + potassium iodide attempted on galena and jamesonite proved to be reliable. In the course of the reaction a thin iridescent membrane formed on the surface, due to the iodide evolved, which could be easily removed with a cloth moistened with a solution of thiosulphate.

The reagent used for the treatment of the gelatine paper: 0.1 g of cinchonin dissolved in water (10 ml) and slightly acidified with nitric acid is dissolved under heating, on dissolution and cooling potassium iodide 0.2 g is added. In the presence of lead a yellow colourization appears. Really speaking the reagent ought not to be suitable for the detection of lead associated with bismuth, as bismuth produces an orange yellow colour with the reagent, however, in the case of sulphide ores the various bismuth minerals (bismuthinite, cosalite, tetradymite and other bismuth tellurides) do not interfere as they are not conductive. By means of the cinchoninous-potassium iodidous reaction metallic bismuth can be detected in different alloys.

### The detection of zinc

Potassium ferrocyanide was generally used for the detection of zinc. Considering that potassium ferrocyanide is not a specific zinc reagent a reagent had to be found with which the latter could be unequivocally detected. On the basis of qualitative as well as quantitative analyses it is known that zinc forms with mercury rhodanide a white zinc mercury rhodanide. Quantitative determination cannot be carried out in the presence of copper, as copper forms a similar compound with the reagent. However, this characteristic is applicable for qualitative examinations. The gelatine paper is permeated with ammonium sulphate and electrolysed and subsequently placed after removing the excess moisture into the reagent solution. A small piece of gelatine paper is first impregnated with ammonium sulphate and then with copper sulphate and also introduced into the reagent solution. The gelatine paper used as blank turns greenish, whereas in the presence of zinc the test paper shows a greyish lilac colour corresponding to the sites containing this ore. The colourization develops slowly.

The following procedure is similarly well applicable: the colour of the dilute cobalt nitrate solution (0.02 per cent cobalt solutin) on mixing with

ammonium mercury rhodanide turns extremely slowly blue. As contrasted with this in the presence of only a very slight amount of zinc a very strong blue colourization is instantaneously produced. The gelatine paper is impregnated with a solution of ammonium sulphate and subsequently on removing the excess moisture electrolysed the paper having previously been immersed into dilute cobalt nitrate or sulphate solution and then the excess moisture again removed the paper is introduced into the reagent solution. The paper shows almost instantaneously on the places corresponding to the granules containing zinc a blue colourization, whereas the blank merely impregnated with ammonium sulphate and cobalt solution remains colourless for a fairly long period turning then slightly blue.

### The detection of silver

Attempts to use one or the most sensitive silver reagents paradimethylamidobenzylidenrhodanine for the detection of silver by the means of electrographical investigations failed. When an acetic solution of the reagent was used to impregnate the test paper the reprint was either blurred or the test-paper dried and did not conduct. Hence the impregnation of the paper with sodium- or potassium bromide and its treatment after electrolysis with a photographic developer proved to be the most satisfactory method.

### B) Structure etching

Structure etching is in addition to local qualitative chemical analyses, another field for the application of electrographical examinations. This procedure is well known and has been much applied for both metallographic and ore texture examinations. Essentially the procedure is as follows: either the examined sample is immersed with its ground polished side into a suitable electrolyte solution and used as anode, as cathode a platinum plate is applied, or the whole procedure is carried out in a platinum dish applied as cathode and the electrolysis accomplished.

If the structure etching is performed with an apparatus also used for electrographical chemical investigations the procedure is far simpler. A filter paper layer impregnated with ammonium sulphate (10 per cent) or ammonium chloride solution is placed onto the aluminum plate used as cathode and the polished section to be examined is put onto this paper layer with its ground side downwards and the electrolysis initiated.

Structure etching produced by electrolysis is particularly suitable in cases in which the ore involved is considerably resistant to the generally used corrosives. Although it is clear that electrolytic etching does not either develop other structures than those produced by other etching means — provided that the investigated ore is not resistant to corrosives — yet the following considerations support its application:

a) the procedure is simpler and more convenient than the usual ones, moreover a relatively even etching is produced on the entire surface of the polished section.

b) the use of various acids and bases and other chemicals applied as corrosives is eliminated. At the structure etchings illustrated on the microphotos ammonium sulphate (10 per cent) could be used in all cases as electrolyte. Whereas, at the etchings done in the usual manner the following corrosives would have been made: for arsenopyrite alkaline hydrogen peroxide and

alkaline potassium permanganate solutions respectively, for bornite an iodic potassium iodide solution, for galena alcoholic nitric acid, for chalcopyrite alkaline potassium permanganate, or concentrated hydrochloric acid or a mixture of concentrated nitric acid and potassium perchlorate, for chalcocite that of concentrated nitric acid or potassium cyanide, for lusonite — famatinite a solution of potassium cyanide, and finally for nickelite one of sulphuric acid with hydrogen hyperoxide or potassium permanganate,

c) its greatest advantage lies in the fact that the extent of the etching can be controlled as desired by regulating the action period and the intensity of current, respectively. In the intervals the progress of the etching can be controlled under the microscope. Both granule-boundary and surface etching can be brought about. The electrolysis is begun at low current rate after a short time the effect is controlled under the microscope, and subsequently — gradually increasing the current intensity — the electrolysis can be continued to the desired extent. Thus the smallest and finest details cannot avoid our attention which later in the course of the etching might disappear.

#### The structure etching of chalcocite (phot. 1—4.)

The electrolysis was carried out for one minute with 1 mA, then for one minute with 2 mA, subsequently for two minutes with 3 mA and finally for another one minute with 4 mA. In the initial stage only the granule boundaries can be detected (phot. 1.), presently they become more pronounced (phot. 2.) finally a perfect granular surface etching is produced (phot. 3.). Phot. 4. shows also a structure etching of a chalcocite.

#### The structure etching of lusonite-famatinite (phot. 5—7.)

In a short time the procedure developed a fine polysynthetic twin lamellar structure on which the translation was also well visible.

#### The structure etching of bornite (phot. 8.)

On bornite structure etching is usually considerably difficult to develop. Electrolytically a prolonged action produced a granular boundary etching.

#### The structure etching of nickelite (phot. 9—10.)

The structure etching was developed with 2—3 mA and 0,6—0,7 V. The translation twin lamellar structure can be very well detected.

#### Structure etching of chalcopyrite (phot. 11—14.)

In the case of chalcopyrite the twin lamellae was developed with 1 mA (phot. 11.) the granule boundary and the twinning on the granular surface

(phot. 12.) with 2 mA (3V) for three minutes, whereas the granule-boundary and twinning illustrated on phot. 13. was produced by electrolysis for five minutes with 0,2 mA, for five minutes with 0,4 mA, for five minutes with 0,6 mA, for one minute with 2,5 mA and finally for one minute with 5 mA. After the etchings the irised film formed on the surface of chalcopyrites, but also in the case of the other minerals can be removed with a short and light polishing on cloth with magnesia.

### Structure etching of galena

(phot. 15—16.)

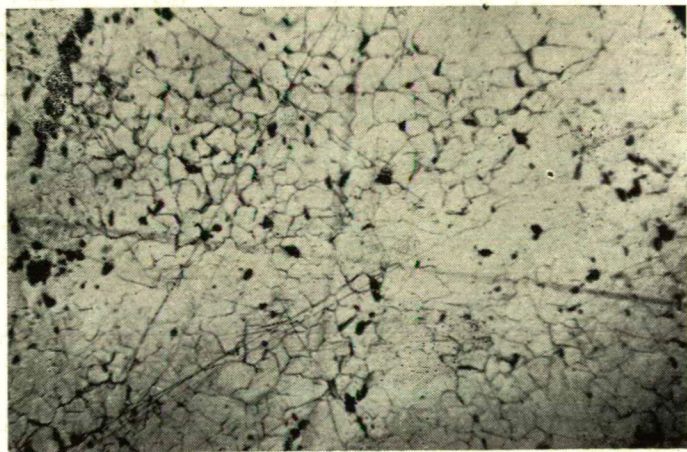
On the surface of galena sometimes irregularly and sometimes regularly arranged unaffected polished surfaces remain (phot. 15.), in the latter case they form a distinct angle with the cleavage direction of galena (phot. 16.).

### Structure etching of arsenopyrite

(phot. 17.)

In the case of arsenopyrite with 2—4 mA a good structure etching can also be developed the granule-boundary and growths zones (twinning lamellar structure) are equally well visible.

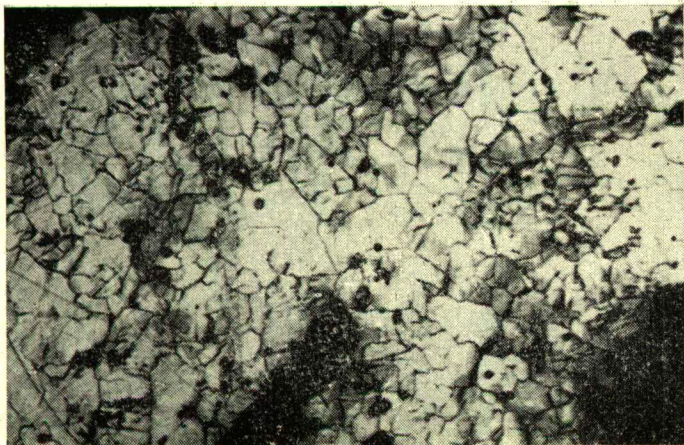
Of course electrolytic structure etching can only be applied with conductive ores as electrographical methodes can also only be applied for qualitative chemical investigations in the case of conductive ores. This represents a certain inhibition, however, only with respect to the point of view of the latter examinations, whereas in the case of structure etching the fact that some granules become etched in the polished section, whilst others, e. g. bismuth minerals, bismuth tellurides and sphalerite remain intact and polished, may even be regarded as characteristic.



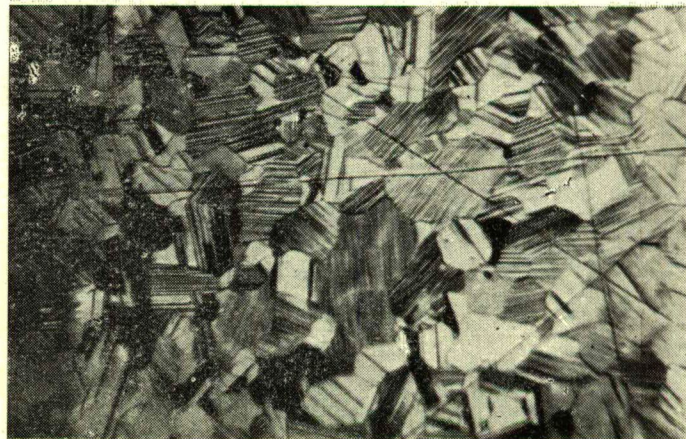
1.

Chalcocite, 70×

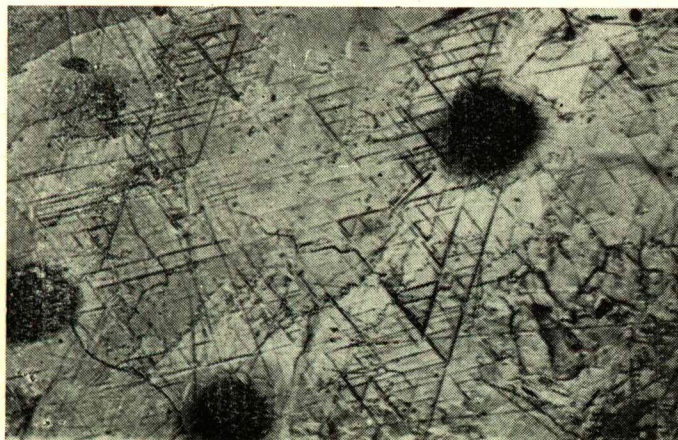




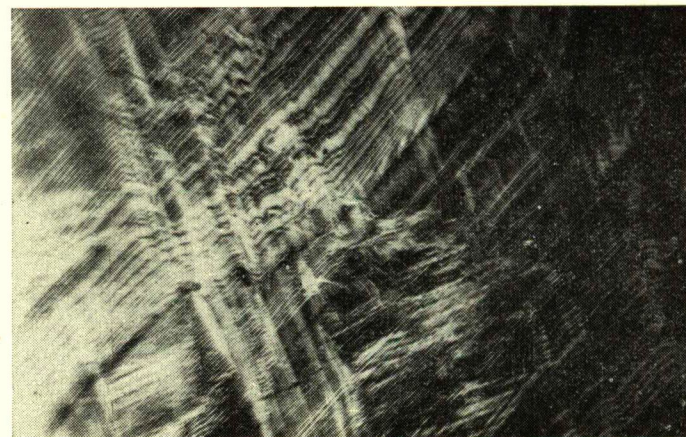
2. Chalcocite, 90  $\times$



3. Chalcocite, Oel imm. 400  $\times$

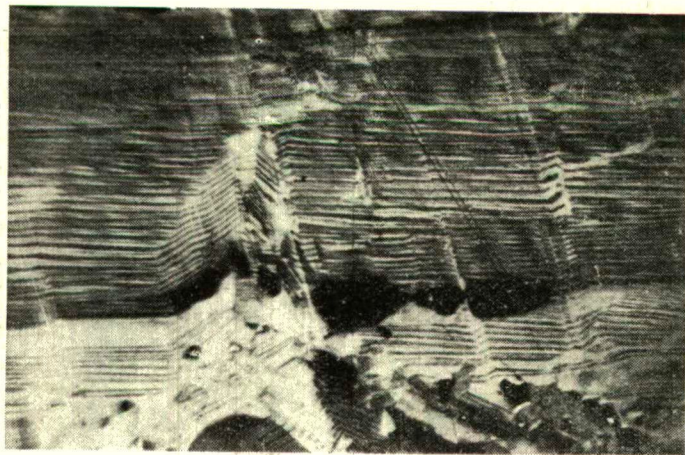


4. Chalcocite, 90  $\times$

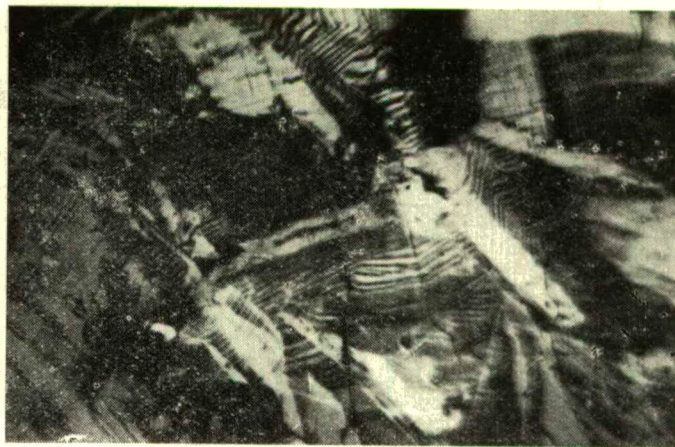


5. Luzonite-famatinite, Oel imm. 400  $\times$

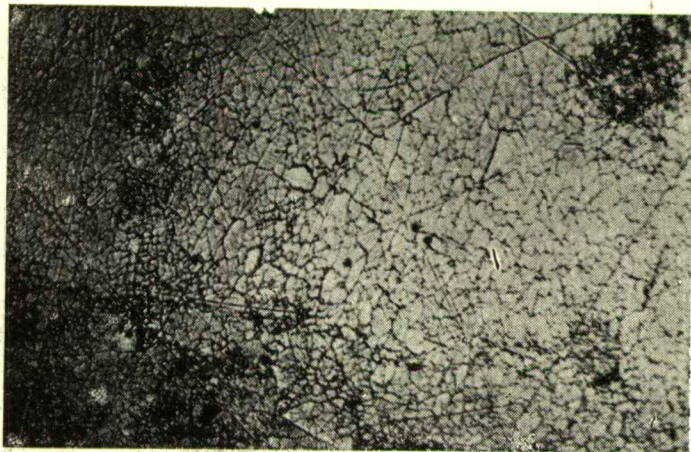




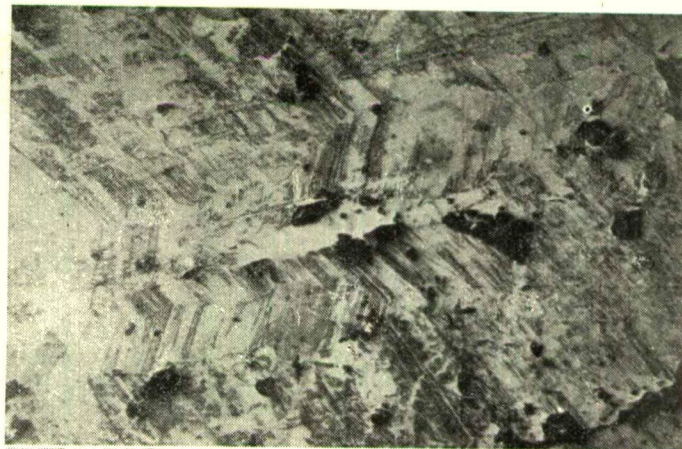
6. Luzonite-famatinite, Oel imm. 400  $\times$



7. Luzonite-famatinite, Oel imm. 400  $\times$

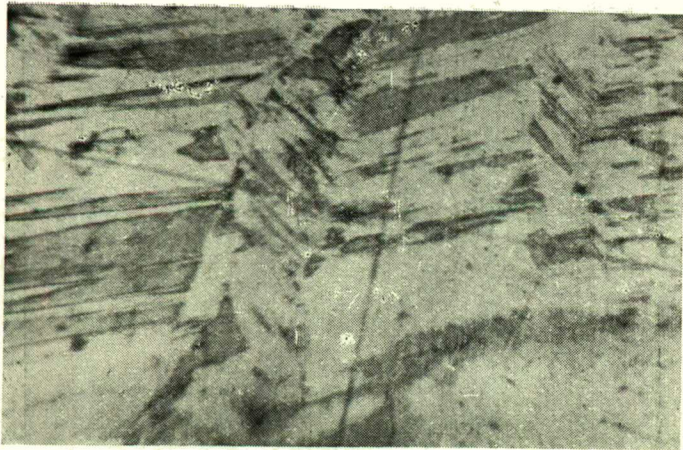


8. Bornite, Oel imm. 400  $\times$

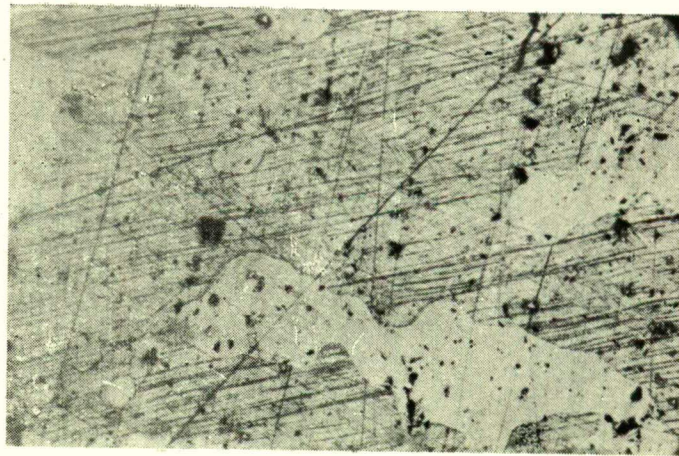


9. Nickelite, 70  $\times$

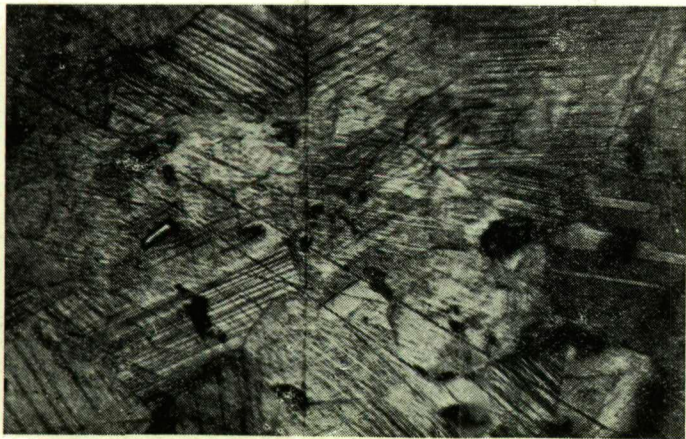




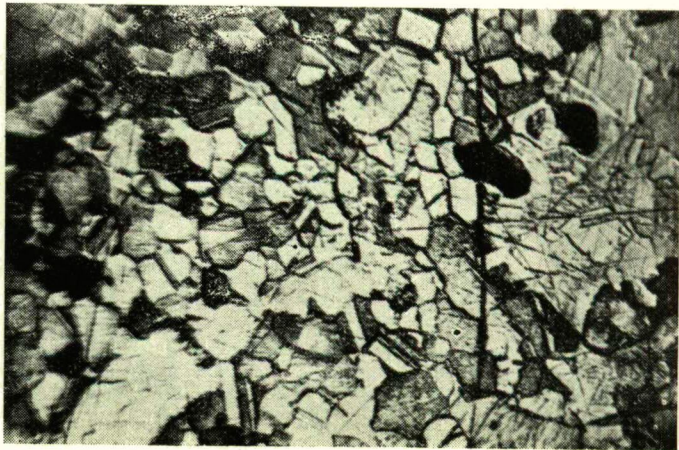
10. Nickelite, 300 X



11. Chalcopyrite, 70 X

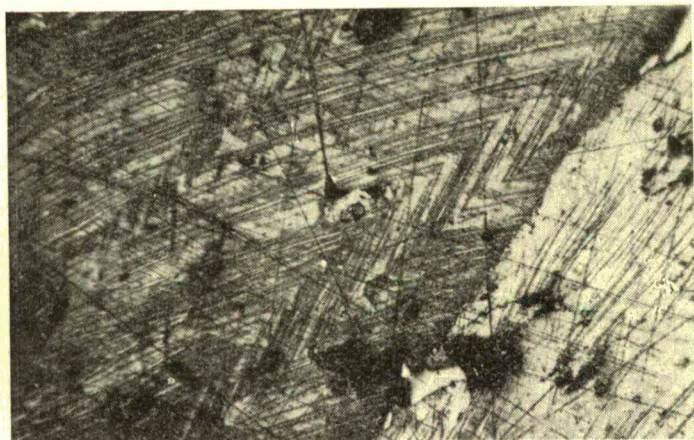


12. Chalcopyrite, Oel imm. 400 X



13. Chalcopyrite, 70 X

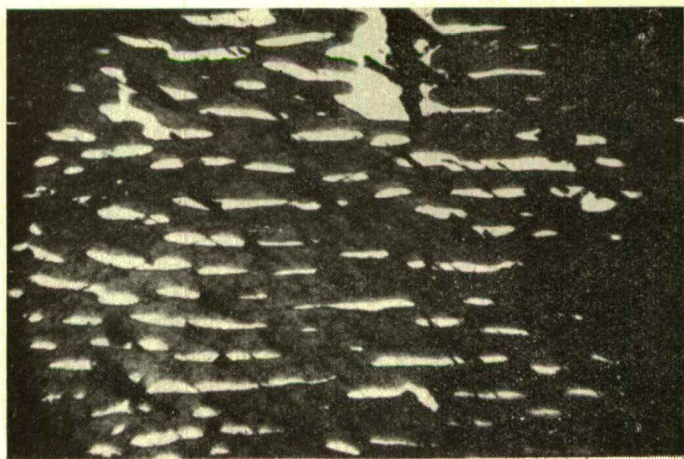




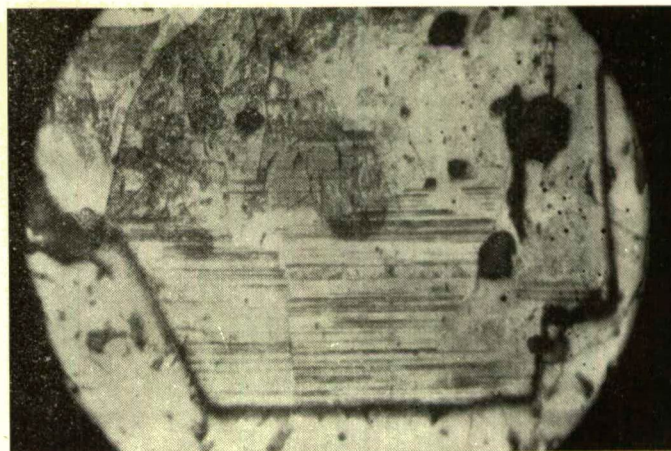
14. Chalcopyrite, 260 X



15. Galena, 260 X



16. Galena, 90 X



17. Arsenopyrite, 100 X

## ЭЛЕКТРОГРАФИЧЕСКИЙ АНАЛИЗ РУДНОЙ ТКАНИ.

— ЮЛИЙ ГРАССЕЛЛИ —

Обнаружению кобальта с  $\alpha$ -нитрозо  $\beta$ -нафтолом мешают железо и медь. Мешающее действие можно устранить, если желатинную бумагу обрабатывать фосфатом натрия, затем иодидом калия, тогда, тиосульфата натрия, потом в реактивный раствор уксусной кислоты. Этим путём мешающее действие меди и железа было совершенно устранено и напр. в арсенопиритах и в лёллингитах можно обнаружить и ничтожные количества кобальта. Вышеупомянутый реагент одновременно пригодится и к обнаружению сернистых мышьяков железа в рудных тканях, поскольку он на желатинной бумаге, пропитанной реагентом, вызывает сейчас же чёрнобурый цвет, отклоняющийся от окраски, вызванной кобальтом. Мышьяк обнаруживается на желатинной бумаге, обработанной нитратом серебра. Для обнаружения свинца и висмута служит реагентная бумага, обработанная раствором иодида калия и цинхонина. Чтобы обнаруживать цинк, реагентная бумага обрабатывается разбавленным раствором нитрата кобальта, потом проводится электролиз и погружение её в раствор роданата аммония. На месте рудных зерн, содержащих цинк, появляется интенсивная синяя окраска.

Другая область применения электрографии — травление структуры. Идущее таким путём травление структуры обладает тем главным преимуществом, что мера воздействия зависит от нашего усмотрения, легко регулируется и, в это время, продвижение травления под микронкопом контролируется. Проведенные этим способом травления структур изображенные на фотоснимках, совершались за несколько минут, при нескольких mA

Table 4.

Tápé	Ca	Mg	Na	K	Fe	Cl	SO <sub>4</sub>	HCO <sub>3</sub>	CO <sub>3</sub>	PO <sub>4</sub>	Cations	Anions
I. 28.	2,0570	0,6474	0,8665	0,0999	0,0029	0,4197	0,7140	2,6200	—	0,0094	3,6737	3,7631
II. 25.	1,3550	0,6148	0,5235	0,0852	0,0114	0,2676	0,5510	2,0140	—	0,0103	2,5899	2,8429
III. 3.	1,5910	0,8981	0,6757	0,1069	—	0,4056	0,6386	2,2945	—	0,0120	3,2717	3,3507
III. 10.	1,8840	0,7939	0,8500	0,1018	—	0,7661	0,7389	2,3150	—	—	3,6297	3,8200
III. 17.	2,3750	1,0295	0,7830	0,1385	—	0,7465	0,8555	2,8760	—	—	4,3260	4,4780
III. 24.	2,0070	1,3440	0,4193	0,0644	0,0028	0,6535	0,7391	2,4580	—	—	3,8375	3,8506
III. 31.	1,4740	0,8284	0,5686	0,1249	—	0,4056	0,4107	2,1840	—	0,0120	2,9959	3,0123
V. 12.	1,7425	0,4989	0,5748	0,0534	0,0025	0,3098	0,4825	2,1790	—	—	2,8721	2,9713
V. 19.	1,9540	0,5695	0,5548	0,0693	0,0111	0,4816	0,5713	2,1900	—	—	3,1587	3,2429
V. 26.	1,8790	0,6025	0,6448	0,1017	0,0122	0,5154	0,5849	2,2150	—	0,0102	3,2402	3,3255
VI. 2.	2,1395	0,8481	0,6604	0,0736	0,0078	0,5437	0,6638	2,4130	—	—	3,7294	3,6205
VI. 9.	1,8043	0,9335	0,9013	0,1018	0,0021	0,6535	0,6399	2,4496	—	—	3,7430	3,7430
VI. 16.	1,5350	0,5493	1,0535	0,1046	0,0011	1,3197	0,4927	1,6597	—	—	3,2435	3,4721
VI. 23.	1,6975	0,6790	0,6309	0,0859	0,0093	0,6451	0,5133	2,0297	0,0600	—	3,1026	3,2481
VI. 30.	1,9700	0,7488	0,5048	0,0816	0,0025	0,4887	0,4448	2,0997	0,1600	—	3,3077	3,1932
VII. 7.	1,4900	0,9433	0,7435	0,0903	0,0025	0,5183	0,5612	2,2396	0,1200	—	3,2696	3,4391
VII. 14.	1,3870	0,8235	1,3143	0,1026	0,0014	1,4254	0,5440	1,6797	0,0600	—	3,6288	3,7091
VII. 21.	2,3645	1,0213	1,0022	0,1770	0,0057	0,7323	0,6570	2,9495	0,2600	—	4,5707	4,5988
VII. 28.	2,8050	1,0874	0,9547	0,0989	0,0028	0,3051	0,8657	3,2594	0,3727	—	4,9488	4,8029
VIII. 4.	2,6300	0,7688	1,3183	0,0788	0,0032	0,4456	0,7392	3,3694	0,1647	—	4,7991	4,7189
VIII. 11.	2,5975	0,6190	1,1526	0,0859	0,0021	0,2992	0,7975	3,1694	0,2100	—	4,4571	4,4761
VIII. 18.	2,4850	0,6338	1,0661	0,1199	0,0011	0,3946	0,7700	2,9243	0,1826	—	4,3059	4,2715
VIII. 25.	2,6150	0,8268	1,0339	0,0934	0,0028	0,2659	0,8349	3,3194	0,1737	—	4,5719	4,5936
IX. 1.	2,7800	0,6232	1,0486	0,1026	0,0007	0,2704	0,7660	3,3195	0,0183	0,0009	4,5551	4,3751
IX. 8.	2,7750	0,5443	1,1891	0,0962	0,0007	0,3543	0,7535	3,2994	0,0183	0,0009	4,6053	4,4264
IX. 15.	2,5725	0,5443	1,0691	0,1141	0,0007	0,3042	0,7327	3,0400	0,0373	0,0034	4,3007	4,1176
IX. 22.	1,9170	0,7635	1,0391	0,0274	0,0029	0,2592	0,7577	2,6756	0,0737	0,0043	3,7499	3,7705
IX. 29.	2,5600	0,3415	0,9574	0,0982	0,0057	0,3183	0,7577	2,8895	—	0,0009	3,9628	3,9664
X. 6.	2,2420	0,3415	0,3900	0,0693	0,0075	0,6592	0,4080	2,4696	—	0,0009	3,0503	2,9377
X. 13.	1,5535	0,3465	0,4526	0,0783	0,0111	0,0732	0,4996	1,8997	—	0,0009	2,4420	2,4734
X. 20.	1,8695	0,6387	0,5078	0,0783	0,0043	0,3972	0,4670	2,2796	—	0,0013	3,0991	3,1451
X. 27.	1,6145	0,5839	0,3883	0,0816	0,0061	0,2914	0,4706	1,9107	—	0,0009	2,6744	2,6736
XI. 3.	1,5250	0,5239	0,3122	0,0368	0,0114	0,1775	0,3684	1,8197	—	0,0009	2,4090	2,3965
XI. 11.	1,4070	0,5139	0,2717	0,0665	0,0093	0,2366	0,2227	1,8097	—	0,0011	2,2684	2,2701
XI. 17.	1,4560	0,5837	0,4669	0,0297	0,0075	0,3042	0,4017	1,8397	—	0,0012	2,5438	2,5468
XI. 26.	1,3350	0,5941	0,4004	0,0448	0,0100	0,1775	0,3455	1,8187	—	0,0017	2,3843	2,3438
XII. 1.	—	0,2607	0,3147	0,0598	0,0064	0,1634	0,4484	1,7400	—	0,0009	—	—
XII. 8.	1,3560	0,5435	0,3583	0,0586	0,0114	0,1887	0,3936	1,7197	—	0,0011	2,3278	2,3031
XII. 16.	1,6090	0,3997	0,4761	0,0304	0,0025	0,2451	0,4858	1,8597	—	0,0007	2,5177	2,5913
XII. 22.	1,6410	0,4745	0,4086	0,0550	0,0204	0,2169	0,4278	1,8898	—	0,0009	2,5995	2,5354
XII. 30.	1,4035	0,6741	0,3352	0,0683	0,0016	0,1977	0,4448	1,7597	—	0,0009	2,4827	2,4031



Table 5.

Szeged	Ca	Mg	Na	K	Fe	Cl	SO <sub>4</sub>	HCO <sub>3</sub>	CO <sub>3</sub>	PO <sub>4</sub>	Cations	Anions
I. 30.	2,2965	0,7648	0,8700	0,0936	0,0018	0,9577	0,7119	2,5099	—	0,0052	4,0327	4,1847
II. 28.	1,8070	0,6924	0,6778	0,0881	0,0029	0,5493	0,7107	2,0599	—	0,0043	3,2682	3,3242
III. 5.	1,8465	0,7266	0,8361	0,0794	—	0,7268	0,6953	2,1299	—	—	3,4886	3,5520
III. 12.	2,2450	0,7889	0,9520	0,1104	—	0,9887	0,7346	2,6100	—	—	4,0963	4,3333
III. 19.	2,2450	0,8686	1,0748	0,1862	—	1,0816	0,6146	2,6698	—	0,0155	4,3746	4,3815
III. 26.	2,2450	0,7143	1,0287	0,6975	0,0079	1,0845	0,6394	2,3600	—	0,0044	4,0934	4,0883
IV. 2.	2,1155	0,6696	0,6939	0,6996	0,0050	0,5493	0,7910	2,1700	—	—	3,5836	3,5103
IV. 6.	1,7670	0,5750	0,4504	0,0721	0,0223	0,3211	0,4788	1,8400	—	—	2,8868	2,6399
IV. 12.	1,5220	0,5679	—	—	0,0105	0,3239	—	1,6400	—	—	—	—
IV. 21.	1,6035	0,5860	0,4256	0,0794	0,0093	0,3521	0,4639	1,6300	—	0,0103	2,7038	2,4563
IV. 28.	1,5790	0,5467	0,5765	0,0512	0,0039	0,5154	0,3455	1,6400	—	0,0017	2,7573	2,5026
V. 5.	1,5085	0,4729	0,4791	0,0503	0,0329	0,6085	0,4208	1,6400	—	—	2,5437	2,6693
V. 14.	1,7180	0,4835	0,7091	0,0880	0,0051	0,4901	0,6457	1,8200	—	—	3,0037	2,9558
V. 21.	1,8815	0,5206	0,3619	0,0462	0,0045	0,3324	0,7138	1,8400	—	—	2,8147	2,8862
V. 28.	1,9545	0,6579	0,4909	0,0469	0,0050	0,5465	0,5530	2,0499	—	—	3,1552	3,1494
VI. 4.	2,0740	0,7044	0,6539	0,0935	0,0057	0,6873	0,6598	2,3399	—	—	3,5315	3,6870
VI. 11.	1,7875	0,7438	0,9252	0,0685	0,0014	0,8592	0,5579	1,9897	—	—	3,5264	3,4068
VI. 18.	1,9995	0,8235	0,9200	0,0780	0,0025	0,8380	0,6869	2,2296	—	—	3,8235	3,7545
VI. 25.	1,8700	0,3842	0,7387	0,0483	0,0054	0,5901	0,5133	1,9696	0,0600	0,0600	3,0466	3,1330
VII. 2.	1,6450	0,7183	0,9013	0,1033	0,0039	0,8310	0,4586	2,0797	—	—	3,3718	3,3693
VII. 9.	1,9520	0,9293	0,8173	0,0969	0,0057	0,7127	0,6374	2,2696	0,1200	—	3,8012	3,7397
VII. 16.	2,2750	0,9211	1,0839	0,1718	0,0078	1,1098	0,6911	2,6295	0,0200	—	4,4596	4,4504
VII. 23.	2,3300	0,9795	1,1222	0,1179	0,0132	1,3296	0,6370	2,4262	0,0600	—	4,5628	4,4528
VII. 30.	2,6725	0,9286	1,2235	0,0839	0,0014	0,7775	0,7631	3,0066	0,2663	—	4,9099	4,8135
VIII. 6.	2,5300	0,6642	1,2517	0,0982	0,0028	0,7318	0,7186	2,8595	0,1010	—	4,5469	4,4109
VIII. 13.	2,6300	0,7061	1,3157	0,0910	0,0035	0,7822	0,7119	2,9095	0,3100	—	4,7463	4,7136
VIII. 19.	2,0775	0,6297	1,4743	0,1575	0,0021	0,7642	0,7119	2,6545	0,1647	—	4,3411	4,2953
VIII. 27.	2,5950	0,5312	1,2426	0,0824	0,0017	0,6758	0,7119	3,0456	0,0737	—	4,4529	4,5070
IX. 3.	2,8495	0,4852	1,4213	0,1120	0,0032	0,6929	0,7161	3,3094	—	0,0009	4,8712	4,7193
IX. 10.	2,9350	0,4548	1,5469	0,1338	0,0021	0,6817	0,7182	3,2371	0,0637	0,0017	5,0726	4,7024
IX. 17.	2,5450	0,4984	1,4574	0,1005	0,0021	0,6282	0,7036	3,0495	0,0283	0,0052	4,6034	4,4148
IX. 24.	2,4800	0,9934	1,1609	0,1242	0,0025	0,6563	0,6828	3,0595	0,0363	0,0023	4,7610	4,4372
X. 1.	2,2860	0,3465	1,2017	0,1120	0,0036	0,6028	0,5579	2,6896	—	0,0060	3,9498	3,8563
X. 8.	1,6635	0,5443	0,5617	0,0680	0,0125	0,2930	0,4829	1,9397	—	0,0017	2,8500	2,7173
X. 15.	1,6710	0,4401	1,1056	0,0772	0,0018	0,5436	0,4413	2,1097	—	0,0009	3,2957	3,0955
X. 22.	1,8635	0,5837	0,7834	0,0839	0,0029	0,6197	0,5453	2,1796	—	0,0018	3,3174	3,3464
X. 29.	1,4650	0,4540	0,4378	0,0724	0,0064	0,4056	0,4266	1,6497	—	0,0052	2,4356	2,4871
XI. 4.	1,3835	0,4294	0,4995	0,0281	0,0104	0,3831	0,3601	1,6397	—	0,0011	2,3509	2,3840
XI. 12.	1,5100	0,4737	0,5626	0,0899	0,0032	0,4296	0,4309	1,8297	—	0,0010	2,6394	2,6912
XI. 19.	1,2290	0,4189	0,5509	0,0417	0,0093	0,4197	0,3539	1,4398	—	0,0010	2,2498	2,2144
XI. 28.	1,6830	0,3391	0,4087	0,0509	0,0050	0,3070	0,4688	1,7397	—	0,0017	2,4867	2,5172
XII. 3.	1,6755	0,3047	0,4686	0,0425	0,0029	0,3437	0,4380	1,7897	—	0,0014	2,4942	2,5728
XII. 9.	1,5120	0,2693	0,4326	0,0670	0,0118	0,3068	0,3872	1,6597	—	0,0014	2,2927	2,3551
XII. 18.	1,8520	0,5988	0,6304	0,0650	0,0011	0,4423	0,6261	2,0697	—	0,0012	3,1473	3,1393
XII. 22.	1,4405	0,5141	0,4178	0,0396	0,0125	0,2282	0,4825	1,6897	—	0,0010	2,4245	2,4014
XII. 30.	1,3480	0,6389	0,3730	0,0645	0,0118	0,2056	0,5235	1,6597	—	0,0007	2,4362	2,3895

Table 6.

Maros	Ca	Mg	Na	K	Fe	Cl	SO <sub>4</sub>	HCO <sub>3</sub>	CO <sub>3</sub>	PO <sub>4</sub>	Cations	Anions
II. 2.	1,9990	0,6424	1,6860	0,0707	0,0052	1,9916	0,2395	2,2041	—	0,0025	4,4033	4,4379
II. 29.	2,0404	1,0722	1,2086	0,0999	0,0093	1,3940	0,7460	2,2747	—	0,0206	4,4304	4,4353
III. 7.	2,7997	0,7986	1,6000	0,1162	—	1,8760	0,9582	2,3149	—	0,0074	5,3145	5,1556
III. 14.	2,9215	1,0082	1,7750	0,0482	—	1,8730	1,2524	2,6035	—	—	5,7529	5,7279
III. 21.	2,4510	0,9630	1,7200	0,1125	—	1,9183	0,9512	2,3635	—	—	5,2465	5,2330
III. 28.	1,3825	0,6189	—	—	0,0015	1,2060	0,7330	2,1235	—	—	—	—
IV. 24.	1,6475	0,5042	0,4480	0,0772	—	0,3761	0,5097	1,6426	—	—	2,6769	2,5284
V. 16.	1,3860	0,8261	0,6990	0,0953	0,0093	0,7915	0,4865	1,6430	—	—	3,0157	2,9210
V. 23.	1,7750	0,7528	0,6380	0,0938	0,0038	0,8817	0,6706	1,7007	—	—	3,2634	3,2530
V. 30.	1,8760	0,6294	0,6430	0,1039	0,0134	0,9183	0,5920	1,7537	—	0,0033	3,2657	3,2723
VI. 6.	1,6470	0,7216	0,6460	0,0823	0,0032	1,0310	0,5543	1,6197	—	—	3,1001	3,2050
VI. 13.	1,5650	0,8784	0,8209	0,0939	0,0035	0,6339	0,6162	1,9797	0,1690	—	3,3617	3,3958
VI. 20.	1,8200	0,6190	1,3308	0,1207	0,0021	1,3056	0,5212	1,9696	0,1100	—	3,8926	3,9064
VI. 27.	1,8125	0,6075	0,9522	0,0729	0,0025	1,3591	0,3422	1,7497	—	—	3,4476	3,4510
VII. 4.	2,0495	0,7988	1,2870	0,0923	0,0011	1,4451	0,6126	2,1396	—	—	4,2287	4,1973
VII. 11.	1,5510	1,5649	0,7165	0,1156	0,0021	0,6592	0,6091	2,5995	0,1200	—	3,9501	3,9878
VII. 18.	2,3820	0,8834	1,5400	0,1366	0,0029	2,2394	0,5989	2,0297	0,0400	—	4,9449	4,9080
VII. 25.	2,4675	0,8333	1,6496	0,1041	0,0140	2,2090	0,6330	1,6317	0,4900	—	5,0685	4,9547
VIII. 1.	2,3950	0,7685	1,2291	0,1194	0,0032	1,4873	0,5304	2,6235	0,0463	—	4,5152	4,6875
VIII. 8.	2,3925	0,6741	1,4169	0,1084	0,0025	1,5682	0,5989	2,3375	—	—	4,5944	4,5046
VIII. 15.	2,4150	0,5082	1,6743	0,0974	—	1,6592	0,5579	2,5096	—	—	4,6949	4,7267
VIII. 22.	2,4505	0,4540	1,6017	0,1035	0,0011	1,4873	0,5100	2,4896	—	0,0003	4,6098	4,4878
VIII. 29.	2,9150	0,4491	1,8056	0,1253	0,0011	1,6583	0,6844	2,6496	0,2647	—	5,2966	5,2550
IX. 5.	3,0750	0,3809	1,6404	0,1667	0,0028	1,5239	0,4996	2,9700	—	—	5,2658	4,9935
IX. 12.	2,9950	0,3425	—	—	0,0032	1,4003	0,5579	2,7595	—	0,0160	—	—
IX. 19.	2,5325	0,7159	1,4165	0,0578	0,0021	1,3803	0,5287	2,4796	0,0637	0,0060	4,7248	4,4583
IX. 26.	2,8310	0,6231	1,6282	0,1233	0,0025	1,5408	0,5079	2,8495	—	0,0010	5,2081	4,8992
X. 3.	2,6190	0,4975	2,0778	0,1143	0,0136	1,8113	0,5329	2,7090	—	0,0010	5,3222	5,0452
X. 10.	2,2800	0,4721	1,6456	0,1701	0,0032	1,5465	0,5079	2,2000	0,0920	0,0010	4,5710	4,3474
X. 17.	2,4550	0,4803	2,1478	0,0882	0,0011	1,8225	1,1407	2,1090	—	0,0010	5,1724	5,0642
X. 24.	1,8545	0,4942	1,1509	0,0744	0,0068	1,1366	0,5828	1,9297	—	0,0060	3,5808	3,6551
X. 31.	1,8655	0,4794	1,0222	0,0997	0,0029	1,1296	0,3955	1,9697	—	0,0017	3,4697	3,4965
XI. 5.	1,6265	0,4442	1,1496	0,0680	0,0029	1,0450	0,4267	1,8397	—	0,0018	3,2912	3,3132
XI. 14.	1,9095	0,5090	1,2293	0,0404	0,0035	1,2200	0,4496	1,9397	—	0,0017	3,6920	3,6610
XI. 21.	2,1240	0,5542	1,1870	0,0670	0,0021	1,4131	0,5371	1,9797	—	0,0017	3,9343	3,9316
XI. 29.	1,7595	0,6741	1,0983	0,0650	0,0029	1,3094	0,4380	1,8597	—	0,0016	3,5998	3,6087
XII. 5.	1,7885	0,3346	0,5809	0,0542	0,0125	0,5627	0,3697	1,8197	—	0,0010	2,7707	2,7731
XII. 10.	1,6225	0,6481	0,6313	0,0627	0,0047	0,7069	0,4140	1,7597	—	0,0015	2,9693	2,8752
XII. 19.	1,6885	0,7934	0,7183	0,0696	0,0021	0,8127	0,5612	1,8497	—	0,0009	3,2719	3,2245
XII. 23.	1,7065	0,5847	0,4174	0,0402	0,0036	0,7099	0,5202	1,7097	—	0,0013	2,7524	2,9411
XII. 31.	1,7440	0,3593	0,4617	0,0629	0,0029	0,4451	0,4963	1,7597	—	0,0009	2,6311	2,7020

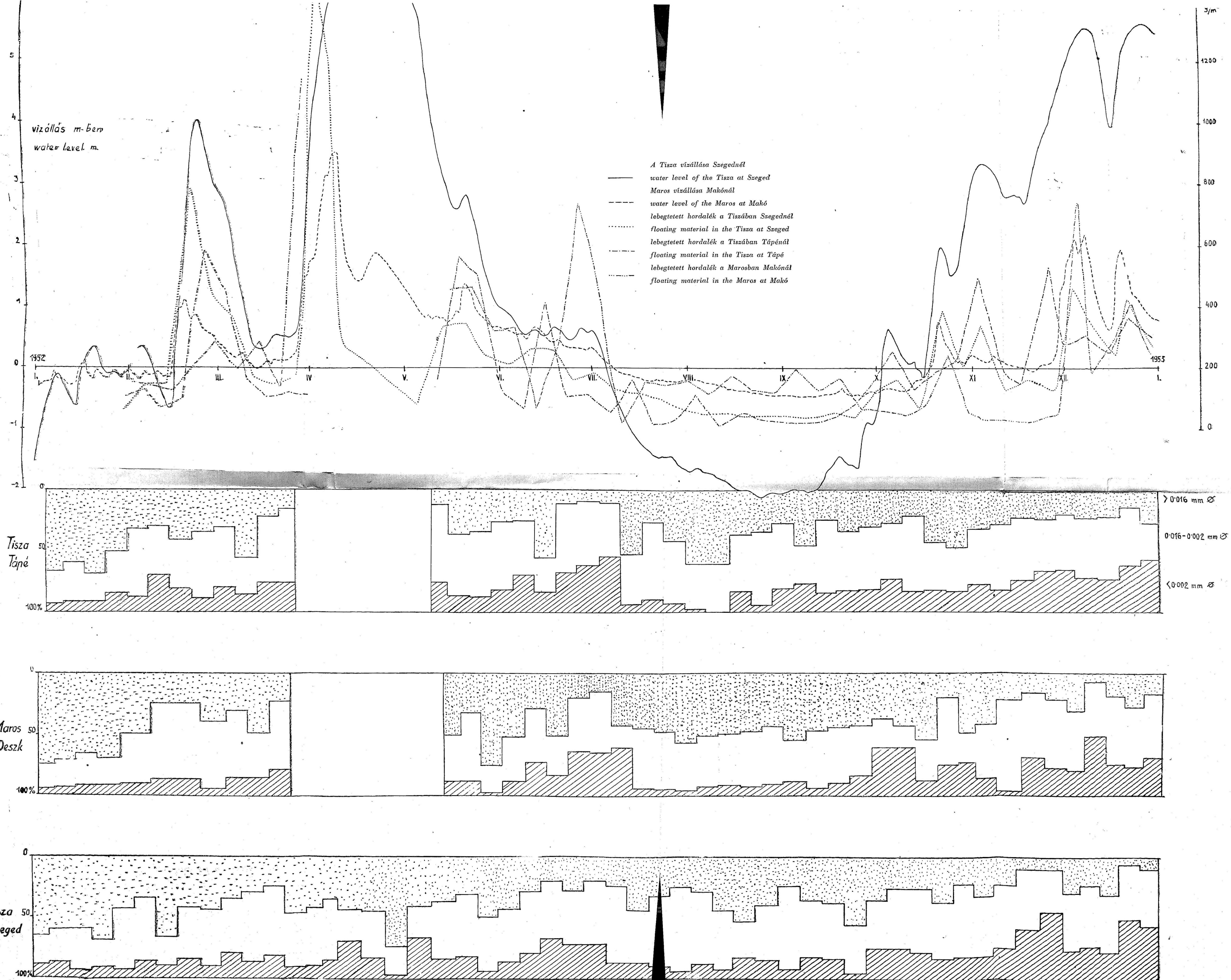


Fig. 8.

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